

# PARRY'S CYCLOPÆDIA OF PERFUMERY

A HANDBOOK

On the Raw Materials used by the Perfumer, their Origin, Properties, Characters and Analysis; and on other subjects of Theoretical and Scientific Interest to the User of Perfume Materials, and to those who have to Examine and Value such Materials

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**MAALI RESIN OIL.**—Maali resin is a white plastic oleo-resin, resembling elemi resin, and is derived from an unknown species of tree. On distillation with steam it yields about 16 per cent. of essential oil, pale green in colour, and having a faint but very pleasant odour recalling that of tea roses. It is semisolid at ordinary temperatures, melting at between 65° and 80°. The crystalline constituent is a sesquiterpene alcohol,  $C_{15}H_{26}O$ , boiling at 260°, melting at 105°, and having a specific rotation  $+18.33^\circ$ .

**MACE.**—The fruit of the nutmeg, *Myristica fragrans*, somewhat resembles a small peach, which as it ripens splits, showing the seed—the nutmeg—surrounded by a bright crimson reticulated arillus. This, stripped off and dried, is the mace of commerce. *Myristica fragrans*, one of the *Myristicaceae*, is indigenous to the Moluccas, more particularly to the Banda and Sunda islands. (See “Nutmegs.”) Mace occurs in dull pale-reddish flattened lobes, which on soaking in water assume the shape of the nutmeg they originally enclosed. It contains from 5 to 12 per cent. of essential oil. The so-called Bombay mace has very little aroma, and is almost useless as a spice or for essential oil. The essential oil of mace is identical with that of nutmeg, and the two oils cannot be distinguished.

**MADOTHECA OIL.**—*Madotheca levigata* (a liverwort belonging to the natural order *Jungermanniaceae*) yields 0.9 per cent. of essential oil (calculated on the air-dried plant) which has a pleasant aromatic odour, recalling that of peppermint. It contains an alcohol of the formula  $C_{10}H_{18}O$ , and has a specific gravity 0.856; specific rotation,  $+72.7^\circ$ ; and acid value, 5.6.

**MAGNOLIA.**—The flowers of many species of magnolia are intensely fragrant, and although essential oils have been prepared from them they are scarcely commercial articles, and the perfumes sold under the name magnolia are practically entirely artificial. The odour of typical magnolia flowers is heavy and “Oriental” in character, recalling a mixture of rose, lemon, lily, and ylang-ylang. The name was given to the genus in honour of Pierre Magnol, a professor of medicine who died in 1715. The species are for the most part natives of mountainous countries. They are particularly abundant in western China, India, and the Indian archipelago. They are also found freely in North America, Mexico, and Japan. The flowers of most of the species are powerfully aromatic. The finest of all the magnolias is *Magnolia*

## P E R F U M E R Y

*grandiflora*, a stately evergreen tree growing in North America to a height of 70 to 100 feet. The flowers are large, cup-shaped, white or pale lemon coloured, with an exquisite fragrance. In America the tree flowers during the greater part of the summer, beginning in May, but in England it does not flower before July, and is usually grown against a south wall, as it is somewhat tender. *Magnolia glauca* is a native of North America, growing in low swampy ground at a little distance from the sea from Massachusetts to Florida and Louisiana, especially in New Jersey and Carolina. It is known in America as the white laurel, swamp laurel, swamp sassafras, sweet bay, or beaver tree. The perfume of the flowers is so powerful that it may be detected at a distance of three miles from the tree. Rabak (*Med. Druggist and Pharm. Review*, 1911, 45, 486) has investigated the essential oil of this species and found it to have a specific gravity 0.924 at 25°; specific rotation, + 3.96°; refractive index, 1.4992 at 25°; acid value, 1.8; ester value, 13; and ester value after acetylation, 28. *Magnolia Kobus* is found in Japan, where it attains a height of about 10 feet. It has a rough bark, which has an odour of camphor, and has very fragrant flowers. The essential oil has been examined by Asahina and Nakamura (*Jour. Pharm. Soc. Japan*, 1908, 322), and is stated to contain cineol, citral, anethol, eugenol, methyl-chavicol, phellandrene, linalol, terpineol, and capric and oleic esters. (See also *Roure-Bertrand Fils, Bulletin*, November, 1907, 25; and *Schimmel's Report*, April, 1908.) For an exhaustive account of other species, see Sawyer ("Odorographia," 2, 474). Artificial magnolia perfumes must be based on a certain amount of natural flower perfume, otherwise their quality is very poor. Jasmine, tuberose, and ylang-ylang are the principal natural perfumes used, together with a little verbena. Benzaldehyde, benzylidene acetone, phenyl ethyl alcohol, and hydroxycitronellal are used, together with storax, balsam of Peru, cinnamic esters, and mousse de chène.

**MAHA PENGIRI GRASS.**—See "Citronella Oil."

**MALE FERN OIL.**—The substance usually known in commerce under the name oil or extract of male fern is not the essential oil, but an oleo-resin containing some essential oil. The modern tendency of perfumers to use the perfume materials of such substances as the lichens and liverworts opens up a possibility for the use of the heavy and characteristic odour of some of the ferns. The so-called male fern *Dryopteris filix mas* (*Aspidium*

*felix mas*; *Nephrodium felix mas*) yields a rhizome which is collected, dried, and extracted, usually with ether, to obtain the oleo-resin which is employed as a vermifuge. The essential oil, which is only obtained to the extent of about 0.025 per cent. to 0.05 per cent., is a pale yellow liquid with an intense odour of the fern. It contains free fatty acids, chiefly butyric acid, and esters of hexyl and octyl alcohols, ranging from the butyric up to the pelargonic acid esters.

• **MANDARIN ORANGE OIL.**—Oil of mandarin orange (or Tangerine orange) was so named on account of the Chinese custom of presenting the orange in question to the mandarins. It is expressed from the peel of *Citrus nobilis* (*Citrus madurensis*), which is grown in Italy, Malta, the Azores, and various other places. The oil when dissolved in ether shows a slight fluorescence, due to the presence of methyl anthranilate. It is a highly odorous oil, used to a small extent in perfumery in certain perfumes of the eau de Cologne type. Its characters are as follows :—

|                  |           |                |
|------------------|-----------|----------------|
| Specific gravity | . . . . . | 0.854–0.859    |
| Optical rotation | . . . . . | + 67° to + 76° |
| Refractive index | . . . . . | 1.4745–1.4770  |

The oil contains from 2 to 4.5 per cent. of non-volatile residue when evaporated on the water bath. The principal constituent is limonene, but small quantities of methyl anthranilate and methyl methyl-anthranilate, and of aldehydes of the fatty series are present. A few years ago Japanese mandarin orange appeared on the market, but it was apparently a distilled oil, and of very little odour value, as distillation ruins all the citrus peel oils.

**MARJORAM.**—Owing to the close botanical and chemical relationships, it will be convenient to deal with marjoram and *origanum* oils together. A good deal of uncertainty has up till recently existed in regard to the true origins of the various *origanum* and *marjoram* oils of commerce. They are derived from various species of *Origanum* (natural order *Labiatae*), and E. M. Holmes has, however, cleared up the confusion (*P. & E. O. R.*, 1912, 332; 1913, 741). The oil known as sweet marjoram is derived from *Origanum majorana*, and according to Holmes (*loc. cit.*) the plant is known in this country as sweet, knotted, or garden marjoram to distinguish it from the wild marjoram, *Origanum vulgare*, which differs from it both in appearance and odour. Holmes considers that *Origanum majorana* is only a variety of *Origanum maru*. In France *Origanum majorana* is

known to botanists and florists as *Marjolaine douce*, the wild marjoram being called *Marjolaine sauvage*. In Germany it is known as *Meiran*. It is supposed to be a native of Mediterranean countries, and has been cultivated as a pot herb from the earliest times, being used for this purpose by the ancient Egyptians. It was introduced into this country from North America in 1573, but it is hardly known in a truly wild state in Europe, and its native country must be regarded as doubtful. Other species were, however, and are still, used in southern Europe. Although still cultivated at the present day in almost all countries for culinary purposes, the oil is chiefly distilled in and imported from Spain. The plant is a small bushy herb, usually about 12 or 18 inches high, with small ovate, stalked, greyish-green, entire, somewhat hairy leaves and small, rounded, stalkless heads of flowers, forming greenish clusters at the top of the stems and upper branches, the small white blossoms being rather inconspicuous and almost hidden among the crowded green bracts. There is a perennial variety of the plant with woody stems, which was cultivated by herbalists in this country in the eighteenth century, and was distinguished by the botanist Willdenow as *Origanum majoranoides*. This is the plant that yields the oil distilled in Cyprus. It is generally recognised that the essential oil of marjoram coming from a definite port or place of manufacture is not always identical in composition or constituents. Origanum oil from Trieste sometimes yields carvacrol, and sometimes thymol, in different samples, and the same occurs in oils imported from Smyrna and from Cyprus. It would appear, therefore, that more than one species is employed in the manufacture of the oil in each district. The oils have been attributed to various species of origanum, but the statements do not afford any definite information in cases in which the botanical authority for the name is not given. Thus there are three different species of origanum bearing the name *Origanum Creticum*, two bearing that of *Origanum Smyræum*, and two bearing that of *Origanum Hirtum*, so that the use of either of these names is of no service for identification purposes unless the name of the botanical authority follows that of the plant, e.g., *Origanum Creticum* Linnæus; *Origanum Creticum* Schousboe; or *Origanum Creticum* Sieber. When these are given, it is possible for the botanist to understand which species is meant, and so far the course is clear. But the matter is further complicated when two different plants are used in the same locality at different times or are

## PERFUMERY

mixed before distillation. Failure of the crop or the exhaustion of the wild plant from careless collection may lead at any time to the substitution of the nearest plant having a somewhat similar odour or similar appearance, and then the identification of the botanical source of the oil can only be settled by the botanical examination of a specimen of the plant actually employed for distillation. It is now known that the character and percentage of the phenols carvacrol and thymol differ in different species, and may possibly do so in the same species under different conditions, and that, as a rule, they do not both occur together in the same species. But with the aid of botanical descriptions and illustrations it should be possible to select and cultivate experimentally those species which give the highest yield, and to determine the conditions of soil or the use of particular manure under which the largest yield may be obtained. Until this is done there is little hope of obtaining anything approaching a uniform oil in commerce. The principal plants from which oil of marjoram has actually been distilled and examined are the following : *Origanum majoranoides* Willd. ; *Origanum onites* Linnæus ; *Origanum maru* Linnæus ; and *Origanum Hirtum*, Link.

According to Gubernatis ("Mythologie des Plantes," vol. ii.), there is a Greek legend in reference to *amarakos*, as they call marjoram, that the youth Amaracus, a page of the King of Cyprus, was carrying a vase containing perfumes, and carelessly allowed it to fall to the ground. He was so frightened that he became unconscious, and was changed into a fragrant plant, which was first named "*sampsuchon*," and afterwards "*amarukos*."

The true marjoram is cultivated to a considerable extent in Spain and in northern Morocco, and in the neighbourhood of Sfax (Tunisia). The plant is dried in the sun, when gathered, and the leaves beaten out.

*Origanum vulgare* Linnæus is found in nearly all European countries. It is indigenous to Norway as far as latitude 66° 16' according to Schuebler, and it is also found in Siberia and central Asia. It is found also in North America. It appears to vary considerably in form, and Rouy ("Flore de France," vol. xi., p. 347) describes five or six varieties of the species found in France. It grows freely on the roadsides, and in the woods on dry mountain slopes. The plant is used not only for medicinal purposes, but for perfumery, especially soap perfumery, and as a condiment.

## P E R F U M E R Y

Other species will be mentioned below when their essential oils are described.

*Oil of Origanum majorana*.—This oil is produced principally in Spain, where the fresh plant yields from 0·3 to 0·4 per cent. of oil (0·7 to 3·5 per cent. on the dried herb). It is a yellowish or greenish yellow liquid of powerful and persistent odour and spicy taste. Its characters are as follows :—

|                  |                |
|------------------|----------------|
| Specific gravity | 0·894–0·912    |
| Optical rotation | + 15° to + 20° |
| Refractive index | 1·4725–1·4765  |
| Acid value .     | Up to 1        |
| Ester value .    | 10–30          |

Three samples, two distilled in Cyprus and one in London, have been examined at the Imperial Institute (*Bull. Imp. Inst.*, 1913, **11**, 50) which were said to be true marjoram oils, but which, according to Holmes, were distilled from *Origanum maru*, and according to Stapf from *Origanum majoranoides* Willd. (According to the *Index Kewensis*, the latter is identical with, and not a variety of, *Origanum majorana*.) These oils had the following characters :—

|                                    | Cyprus (1). | Cyprus (2). | London.   |
|------------------------------------|-------------|-------------|-----------|
| Specific gravity . . . . .         | 0·899       | 0·912       | 0·888     |
| Optical rotation . . . . .         | + 14·2°     | + 3·45°     | + 13° 15' |
| Saponification value . . . .       | 6·4         | 8·25        | 12·8      |
| Solubility in 80 per cent. alcohol | 1 in 1·3    | 1 in 1      | 1 in 8–9  |

Cyprian *origanum* oil will be referred to later.

Sweet marjoram oil contains, according to Biltz (*Berichte*, 1899, **32**, 995), about 40 per cent. of terpenes, principally terpinene, and terpineol. Terpinenol is also present, and possibly borneol and a small quantity of esters.

*Oil of Origanum Vulgare*.—The dried herb yields from 0·15 to 0·4 per cent. of essential oil of powerful aromatic odour. Its specific gravity varies from 0·870 to 0·910, and its optical rotation is about – 35°. According to Jahns (*Arch. du Pharm.*, 1880, **216**, 277), the oil contains traces of phenols, but not more than 0·1 per cent.

Angelescu, however (*Gazzetta*, 1922, **52**, i., 157), gives figures for this oil in disagreement with the conclusion of Jahns. Three

## P E R F U M E R Y

samples of *Origanum vulgare* obtained in different parts of Italy were distilled, with the following results :—

|                          | Rome.     | Valle d'Inferno. | Sicily.   |
|--------------------------|-----------|------------------|-----------|
|                          | Per cent. | Per cent.        | Per cent. |
| Yield . . . . .          | 0.204     | 0.072            | 1.106     |
| Thymol . . . . .         | 6.7       | 2.2              | 50        |
| Free alcohols . . . . .  | 15.4      | 12.86            | 4         |
| Esters . . . . .         | 2.63      | 2.56             | 0.85      |
| Sesquiterpenes . . . . . | 12.5      | —                | —         |

The botanical source of these plants may, of course, have been incorrectly ascertained, as the difference in the composition of the oils is so great.

Pellini (*Ann. de Chim. Applic.*, vii., 3) considers that Sicilian oil is the product of *Origanum virens* var. *Siculum*. He finds it to have a specific gravity 0.924 to 0.932; optical rotation,  $-1.54^{\circ}$  to  $-1.66^{\circ}$ ; phenols, 49 to 50 per cent., consisting principally of thymol.

*Oil of Origanum Dictamnus*.—This oil is of yellow colour, and has a strong odour of pulegone. It has a specific gravity about 0.933; optical rotation,  $+3^{\circ}$ ; and contains about 85 per cent. of pulegone.

*Oil of Origanum Creticum*.—An oil distilled in Sicily, probably from *Origanum Creticum*, has been examined by Umney and Bennett (*Pharm. Jour.*, 1905, 75, 860). They found it to have a specific gravity 0.920, to be optically inactive, and to contain 44 per cent. of phenols, mainly carvacrol. The origanum oil distilled in Crete must be regarded as of uncertain botanical origin, and is probably distilled from more than one species.

*Oil of Origanum Hirtum*.—It is probable, but not certain, that the origanum oil entering into commerce *via* Trieste is the distillate, in the main, of *Origanum Hirtum*. The oil (of authentic origin) has been examined by Jahns (*Arch. der Pharm.*, 1879, 215, 1). It has a pungent, thyme-like odour, and a biting, persistent taste. When freshly distilled it is of a golden-yellow colour, which deepens on exposure to air. The yield is about 2 to 3 per cent. on the dry herb. The oil has a specific gravity 0.940 to 0.980; optical rotation,  $-1^{\circ}$  to  $+2^{\circ}$ ; and contains 60 to 85 per cent. of carvacrol. Pickles, however (*Bull. Imp. Inst.*, 1911, 9, 388), has reported on an oil which appears to have been

## P E R F U M E R Y

distilled from the same plant, the yield being 3·3 per cent., and which had a specific gravity 0·944; optical rotation,  $+ 0^{\circ} 24'$ ; and contained no carvacrol, but about 64 per cent. of thymol. Three samples of the oil distilled in the Dalmatian islands were found to be similar to the oil examined by Pickles, and, according to Giessler (*Schimmel's Report*, October, 1911, 63) the plant was *Origanum Hirtum* var. *albiflorum*. Possibly the oil described by Jahns was not from this species at all.

*Smyrna Origanum Oil*.—The oil of *origanum* distilled in Asia Minor and probably elsewhere, enters into commerce *via* Smyrna. It is the distillate of *Origanum onites* (*O. Smyrnæum*). The dry herb yields 1·4 to 2·4 per cent. of oil. It is of a golden yellow to brown colour, and has an odour recalling that of linalol. It has the following characters:—

|                  |       |                                 |
|------------------|-------|---------------------------------|
| Specific gravity | . . . | 0·895-0·965                     |
| Optical rotation | . . . | $- 1^{\circ}$ to $- 15^{\circ}$ |
| Refractive index | . . . | 1·4950-1·5250                   |

It contains from 15 to 75 per cent. of phenols, usually from 25 to 45 per cent., of which the greater part is carvacrol, with some thymol, from 20 to 50 per cent. of linalol, cymene, an olefinic terpene, and probably pinene and camphor. Cedrol has been reported in a sample of this oil, but it was probably due to adulteration with cedar wood oil.

*Syrian Origanum Oil*.—This is probably obtained chiefly from *Origanum maru*. It is a highly aromatic oil containing from 50 to 75 per cent. of phenols, which have been reported as entirely carvacrol, or entirely thymol, or a mixture of the two (*Schimmel's Report*, April, 1907, 73; 1911, 63). It has a specific gravity 0·930 to 0·977; optical rotation,  $0^{\circ} 50'$  to  $1^{\circ} 35'$ ; and is usually soluble in 2 to 3 volumes of 70 per cent. alcohol.

*Cyprus Origanum Oil*.—The botanical origin of the oil which is distilled in Cyprus in fairly large quantities is still a matter of doubt. Cennadius (Pickles, *Jour. Chem. Soc.*, 1908, 93, 862) regards the plant as *Origanum onites*; Holmboe (*ibid.*) regards it as *Origanum dubium*, a subspecies of *Origanum maru*; whilst E. M. Holmes (*Pharm. Jour.*, 1907, 79, 378; *P. & E. O. R.*, 1913, 4, 41) considers it to be *Origanum majoranoides* Willd., which he regards as a variety of *Origanum maru* (*vide supra*). The plant grows wild in the north-western part of the island. The distillation commences in June or July, when the seeds are mature, and lasts until the middle of December. The oil is reddish in colour, and is often erroneously called oil of thyme. It has a



specific gravity 0.862 to 0.967 ; is optically inactive or very slightly dextrorotatory ; and contains from 70 to 85 per cent. of phenols, principally carvacrol. According to Francis, the phenols are principally thymol, but this statement does not appear to be correct. Pickles (*Jour. Chem. Soc.*, 1908, **93**, 862) states that a Cyprian oil examined by him contained traces of isobutyric acid, a phenol which was probably hydroxy-methoxy-cymene, carvacrol, cymene, menthol, camphor, and a terpene which has been provisionally named origanene.

**MARONIOL.**—This is the name given by Jeancard and Satie to an alcohol which they claimed to have isolated from Guiana sandalwood oil (*P. & E. O. R.*, 1911, **2**, 79). The substance boiled at 155° to 159° at 20 mm. ; had a specific gravity 1.0378 at 23° ; and an optical rotation, — 6°.

**MASSOY BARK OIL.**—Various barks have from time to time been found in commerce under the name massoy or massoi bark. The true bark is the product of *Massoia aromatica*, a native of New Guinea. According to Wicsner, *Cinnamomum xanthoneuron* is identical with *Massoia aromatica*, but this is unconfirmed. Schimmel & Co. distilled a bark known as massoy bark from New Guinea, but which E. M. Holmes (*Pharm. Jour.*, 1888, **iii.**, 19, 465 and 761) found very similar to the bark of *Culilabanus Papuanus*, and obtained from 6 to 8 per cent. of a heavy essential oil, having a pleasant aromatic odour recalling that of cloves and nutmegs. Its specific gravity was 1.040 to 1.065. It contains about 70 to 75 per cent. of eugenol, and some safrol. The terpenes pinene, limonene, and dipentene were also present.

**MASTIGOBRYUM OIL.**—A few of the liverworts (*N.O. Jungermanniaceæ*) yield aromatic oils. According to Müller (*Chem. Zentral.*, 1905, **ii.**, 768) *Mastigobryum trilobatum* yields about 1 per cent. (on the dry plant) of a yellow-orange essential oil, which has an odour recalling those of sandalwood, cedarwood, and pine needles. The oil has a specific gravity about 0.945 (exceptionally, 0.975) ; an optical rotation about — 13°, and contains a terpene and some unidentified constituents.

**MAY CHANG.**—See "Litsea Oil."

**MEADOWSWEET, OILOF.**—*Spiræa ulmaria*, the "meadow-sweet" of the countryside, is a common plant in England, especially on the banks of streams and in moist pastures and woods. The flower buds, on distillation with water, yield about 0.25 per cent. of an essential oil of great fragrance. The oil contains

## P E R F U M E R Y

salicylic aldehyde,  $C_6H_4(OH)(COH)$ , as its principal constituent. It also contains a terpene, methyl salicylate, vanillin, and heliotropin. Salicylic aldehyde (*q.v.*) is made artificially, and is used to reproduce the meadowsweet odour.

**MECCA BALSAM.**—See “Balm of Gilead.”

**MEI RHOA.**—This plant (also spelt *Mei Hwa*) is one of the most admired and beloved plants grown in China. It is the so-called “prunus” or “hawthorn.” The flowers have an exquisite odour, and are particularly esteemed on account of the fact that the blooms appear in winter. It is largely used as a perfumed decorative in fashionable saloons. The highly valued (so-called) ginger jars of the K’ang-hsi (Kang-he) period of Chinese porcelain are frequently decorated with the prunus flower with a background to resemble cracked ice. These were used by the rich to send to their friends as New Year presents, filled with the finest tea, the decoration being symbolical of the coming of spring, with the prunus blossoms falling on the already cracking ice.

**MELILOT OIL.**—The dried flowers of *Melilotus officinalis* (N. O. *Leguminosae*) yield 0.015 per cent. of essential oil of highly aromatic odour. The only constituent so far detected is coumarin.

**MELISSA, OIL OF.**—The plant *Melissa officinalis* is indigenous to the northern Mediterranean littoral and western Asia. It is cultivated in northern America. The plant has a lemon odour, recalling that of a mixture of lemongrass and citronella. On distillation the amount of oil obtained is so small that, in spite of its beautiful odour, it is scarcely ever seen in commerce. But as a demand exists for oil of melissa, or “oil of balm,” as it is frequently termed, the supply of something to answer the name also exists. Melissa oil when met with in commerce to-day is practically invariably merely a distillate of lemon oil, with or without a little lemongrass or citronella oil, over the leaves of the plant. Figures published for this oil must be taken with considerable reserve. *Schimmel & Co. (Bericht, October, 1894, 37)* examined two samples from the fresh herb and give the following figures for them:—

|                  | At commencement of<br>flowering. | In full<br>flower. |
|------------------|----------------------------------|--------------------|
| Specific gravity | 0.924                            | 0.894              |
| Optical rotation | + 0° 30'                         | 0°                 |
| Yield            | 0.01 per cent.                   | 0.1 per cent.      |

**MENTHENONE.**—This ketone, of the formula  $C_{10}H_{16}O$ , has

## P E R F U M E R Y

been isolated by *Schimmel & Co.* from Japanese peppermint oil (*Bericht, Schimmel & Co.*, October, 1910, 79). It is a highly aromatic liquid having the following characters:—

|                            |                      |
|----------------------------|----------------------|
| Specific gravity . . . . . | 0.9382               |
| Boiling point . . . . .    | 235°–237° at 752 mm. |
| Optical rotation . . . . . | + 1° 30'             |
| Refractive index . . . . . | 1.4844               |

It yields a semicarbazone which forms two modifications, one melting at 224° to 226°, and the other at 171° to 172°. The oxime melts at 107° to 108°.

**MENTHOCITRONELLOL.**—This alcohol, also known as menthonyl alcohol  $C_{10}H_{20}O$ , is a body of delicate rose odour, and is prepared as follows. *Lævo*-menthone is treated with hydroxylamine, and the resulting oxime is brought into contact with strong sulphuric acid, which converts it into isomenthone oxime. Phosphorus trichloride dissolved in chloroform is added, when hydrochloric acid is evolved and menthonitrile results. This is reduced by sodium to menthonylamine, which is converted into menthocytronellol by means of sodium nitrite (reacting with the oxalate). Menthocytronellol has a specific gravity 0.831; optical rotation, + 2°; refractive index, 1.4471; and boiling point about 100° at 7 mm.

**MENTHOL.**—This body has been known for some centuries in a more or less crude form, but it was not until early in the nineteenth that it was subjected to any systematic chemical examination. Dumas, who analysed it in 1833, stated that “the camphor of peppermint oil only differed from ordinary camphor by two atoms of hydrogen.” In 1839, Walter established the formula for menthol as  $C_{10}H_{20}O$ , which we know to-day to be the correct formula. In 1863, Oppenheim recognised that menthol was an alcohol, and since then numerous chemists have engaged in researches in order to elucidate the constitution of this compound. Menthol  $C_{10}H_{19}OH$  as it occurs in commerce is the characteristic solid alcoholic constituent of peppermint oil, from which it separates in fine crystals on cooling. Theoretically, seven isomeric menthols are possible, of which two are primary, two secondary, and three tertiary alcohols. The two primary alcohols have not so far been definitely characterised. Of the two secondary menthols, one is the menthol of commerce, whilst the second is identical with tetrahydrocarveol, which has not been found in nature, but has been prepared synthetically. The tertiary

## P E R F U M E R Y

menthols have, possibly, been prepared in a more or less pure condition, but it is impossible at present to describe them with any degree of accuracy. There are, of course, further isomeric menthols depending on optical activity; apparently at least eight optically active varieties of natural (secondary) menthol are capable of existence on account of the number of asymmetric carbon atoms contained in the molecule.

Natural menthol of commerce is the product of Japanese peppermint oil (see "Peppermint Oil"), which is far richer in the alcohol than any other of the peppermint oils. In fact, at ordinary temperatures this oil forms a crystalline magma. When the natural oil is cooled, about half its menthol is separated in the crystalline form and is separated off. The liquid oil resulting from this separation is known as "dementholised" peppermint oil, but it still contains from 40 to 45 per cent. of menthol, and up to 12 or 15 per cent. of esters of menthol. The latter yield menthol by saponification, and the oil will then deposit more menthol by sufficient freezing.

The melting point of menthol has been found to vary according to the source of the menthol, that from Japanese peppermint oil melting at  $43^{\circ}$  to  $44.5^{\circ}$  after repeated crystallisations. It is probable that this varying melting point is due to the presence of varying quantities of the isomers (either structural or stereoisomeric) of menthol present.

There is no doubt that commercial menthol, extracted from Japanese peppermint oil, consists in the main of substantially a single chemical individual, which is normal laevorotatory menthol, having, in its purest form, the following characters:—

|                   |           |                                  |
|-------------------|-----------|----------------------------------|
| Melting point     | . . . . . | $44^{\circ}$ – $44.5^{\circ}$    |
| Boiling point     | . . . . . | $215^{\circ}$ – $216^{\circ}$    |
| Specific rotation | . . . . . | — $49^{\circ}$ to — $50^{\circ}$ |

The melting point of menthol has, as above mentioned, been recorded by different observers at figures which vary by several degrees. Some light has been thrown on the matter by F. E. Wright (*Jour. Amer. Chem. Soc.*, 1915, 39). He states that menthol crystallises in four different forms, which he terms a, b, c, and d. Of these, the "a" form is the most stable, and the other forms revert to the "a" form eventually. He states that the "a" form melts at  $35.5^{\circ}$ , the "c" form at  $33.5^{\circ}$ , and the "d" form at  $31.5^{\circ}$ .

It is exceedingly difficult, however, to understand the meaning of these "forms," and it is possible that traces of isomers or other

substances are concerned in the matter. And Wright's results do not assist much in the question of the chemistry of menthol. Further, as pure levorotatory menthol melts at  $44^{\circ}$  to  $44.5^{\circ}$ , it is clear that even in his "a" form he had not a perfectly pure substance.

The recent work of J. Pickard and Littlebury (*Jour. Chem. Soc.*, 101, 109) is of considerably more importance. Starting from the mixture of alcohols which Brunel (*Comptes Rendus*, 137, 1288) had obtained by the reduction of thymol, they isolated from it about 60 per cent. of isomeric menthols, and by means of fractional crystallisation of the zinc and magnesium salts of the phthalic acid esters they succeeded in separating the alcohols into at least two separate compounds. Of these, one was optically inactive menthol melting at  $34^{\circ}$ , and the other was a compound termed "neo-menthol," which melted at  $51^{\circ}$ . These two bodies have the following characters :—

|   | <i>i</i> -Menthol.            | <i>neo</i> -Menthol.          |
|---|-------------------------------|-------------------------------|
| • Melting point . . . . .                 | $34^{\circ}$                  | $51^{\circ}$                  |
| Boiling point at 16 mm. . . . .           | $103^{\circ}$ – $105^{\circ}$ | $103^{\circ}$ – $105^{\circ}$ |
| Melting point of phthalic ester . . . . . | $129^{\circ}$ – $131^{\circ}$ | $175^{\circ}$ – $177^{\circ}$ |

It is probable that this *i*-menthol is the optically inactive variety of the natural levomenthol of peppermint oil, since, by means of the brucine salts of its phthalic ester, it can be separated into *larvo*-menthol (melting point,  $42^{\circ}$ ; specific rotation,  $-48.7^{\circ}$ ) and *dextro*-menthol (melting point,  $40^{\circ}$ ; specific rotation,  $+48.15^{\circ}$ ).

In the same way, neo-menthol can be separated into its optically active varieties.

Commercial menthol, therefore, probably consists in the main of normal levorotatory menthol, with traces of optically inactive menthol of melting point considerably below that of its optically active variety, and possibly traces of other isomers. The active neo-menthols are both liquid at ordinary temperatures.

The statement recently made in an English journal that the synthetic liquid menthol is chemically identical with the natural article is, of course, only to be accepted subject to such limitations as have been indicated above.

The following alleged isomers of natural (secondary) menthol have been claimed to exist :—

(1) By reducing *d*-menthone, Beckmann prepared an "iso-menthol" melting at  $79^{\circ}$  to  $81^{\circ}$ , and having a specific rotation  $+2^{\circ}$ .

## PERFUMERY

(2) By reducing pulegone, Haller and Martine (*Comptes Rendus*, 1905, 140) obtained laevorotatory menthol identical with natural menthol, melting at  $43^{\circ}$  to  $44^{\circ}$ , and having a specific rotation  $-46^{\circ} 40'$ , and two other isomers, which they termed  $\alpha$ -pulego-menthol (melting point,  $84^{\circ}$  to  $85^{\circ}$ ; specific rotation,  $+30^{\circ}$ ) and  $\beta$ -pulego-menthol (liquid; specific rotation,  $+2^{\circ} 36'$ ).

(3) Kondakow and Bachtschiew, by reducing the menthone found in oil of buchu leaves, obtained a menthol melting at  $38^{\circ}$  to  $39^{\circ}$ , and having a specific rotation  $+32^{\circ} 37'$ . These chemists also obtained an amorphous substance, which they consider to be a menthol, which solidifies at  $-10^{\circ}$ .

(4) Brunel (*Comptes Rendus*, 1903, 1288), by the reduction of thymol, obtained  $\alpha$ -thymomenthol, melting at  $-5^{\circ}$ , and  $\beta$ -thymomenthol, melting at  $28^{\circ}$ .

(5) Wright (*Jour. Amer. Chem. Soc.*, 1915, 39) claimed to have isolated four "forms" of menthol (see above) from the commercial substance.

(6) Pickard and Littlebury (*Jour. Chem. Soc.*, 1901, 109), working on Brunel's mixture from thymol reduction, obtained optically inactive menthol, melting at  $34^{\circ}$ , and neo-menthol, melting at  $51^{\circ}$  (see above). The inactive menthol was resolved into its optical isomers, both of which melted at about  $43^{\circ}$ .

Vavon and Coudere (*Comptes Rendus*, 1924, 179, 405) regard ordinary menthol and neomenthol as the *trans*- and *cis*- forms respectively of 1-methyl-4-isopropylhexan-3-ol.

The synthetic menthol of commerce is found in two modifications. Of these, the solid synthetic menthol melts at about  $28^{\circ}$ , and boils at about  $214^{\circ}$ . It is optically inactive. A liquid synthetic menthol is also obtainable. They are in all probability mixtures of various of the isomeric menthols.

Müller has taken out a German patent (376474, April 1st, 1921) for preparing menthol from pulegone.

One kilogram of Spanish oil of pennyroyal is dissolved in five times its weight of ether. A little water is added, and the whole thoroughly cooled in a powerful freezing mixture.

Metallic sodium (0.8 to 1 kg.) is then gradually added at such a rate that hydrogen is not too rapidly evolved, and the temperature does not rise above  $+5^{\circ}$ . More water may be carefully added, as necessary. When all the sodium has been dissolved, the aqueous layer is removed and the ether solution is washed neutral. The oil remaining after distilling off the ether may be rectified *in vacuo* or distilled in steam. From an oil of pennyroyal

with specific gravity 0.9400 and optical rotation  $+20^\circ$  there is obtained by this method, in 80 per cent. yield, an oil of peppermint odour which has specific gravity 0.9114 at  $15^\circ$ ; optical rotation,  $-14^\circ$ ; ester content, 3 per cent. It contains 70 per cent. of menthol (total) and is soluble in 2.3 parts of alcohol (70 per cent. by volume). The oil is water white, and is described as having a very fine peppermint odour and taste, mild, and with a strong cooling effect on nose and mouth.

The same process applied to pure pulegone yields an oil which crystallises on cooling and has all the properties of menthol.

The reduction of pulegone (but not of oil of pennyroyal) to menthol has previously been described by Bechmann and Pleissner (*Annalen*, 1891, **262**, 30), but they used *anhydrous* ether, and obtained only 40 per cent. of the theoretical yield. All other reduction methods, either with sodium and alcohol or by catalytic processes, led to an entirely different result. The menthol is obtained in only small yield, and, instead of being strongly laevorotatory like natural menthol or the above product, is dextrorotatory or only feebly laevorotatory. Only *l*-menthol has the true taste and odour of the natural substance. The *d*-isomer has more of a camphor—or borneol—flavour and smell, and cannot, therefore, be used in place of natural menthol.

The process described above is amenable to several modifications. The caustic soda produced during the reduction may be neutralised as formed. This may be accomplished by addition of acetic acid to the water before mixing it with the ether. The sodium may also be replaced by an equivalent quantity of metallic potassium or calcium.

The most recently patented process for the artificial production of menthol is the following, the complete specification of which, dated August 21st, 1924 (No. 220953), has been issued through the International Convention. It is for the preparation of thymol and menthol, by Geza Austerweil, of Boulogne-sur-Seine, France. The characteristic feature of the process is that *p*-cymene is nitrated, the resultant nitrocymene is dissolved in concentrated sulphuric acid (not over 97 per cent. strength) and electrolysed into *p*-aminothymol with a great excess of current, great cathodic current density, and protection from contact with air; the amino group is then eliminated from the product by diazotation and reduction, and the thymol is steam distilled, and, after drying, reduced to menthol by means of hydrogen under high pressure, with nickel as a catalyst and with brisk stirring.

## PERFUMERY

The thymol thus obtained is reduced with hydrogen at high pressure over nickel as a catalyst to inactive menthol, and the crude menthol thus obtained is transformed into crystalline menthol either through its phthalic acid salt, or by oxidising it to menthone and again reducing it.

*Examples.*—*p*-Cymene obtained from monocyclic terpenes as described in the specification of the Patent No. 206848, granted to L. Peuffaillit and G. Austerweil, or by any other method, is dissolved in its own weight of concentrated sulphuric acid, cooled to 0°, and nitrated with a mixture of 1 part of nitric acid and 2 parts of sulphuric acid, with a little over the theoretical amount of nitric acid to avoid the raising of the temperature above 5°. The mixture is well stirred during nitration, and finally poured into 6 to 8 parts of water cooled to about 0°. The 2-nitro-*p*-cymene deposited as a brown oil is washed and cleaned by steam distillation and the distillation products floating on the condensed water are separated and may be used again for a further nitration. The 2-nitro-*p*-cymene itself is dried and dissolved in concentrated sulphuric acid of a strength over 95 per cent.

Such an 8 per cent. solution of nitrobenzene sulphonic acid is electrolysed. For this purpose it is placed in a cathode chamber in a vessel made of porous earthenware, and covered with molten paraffin. This vessel is put in an anode chamber filled with 75 per cent. sulphuric acid and heated. The electrolysis is carried out at 60° with a cathode density of 8 to 15 amperes per square decimetre, and 5 to 6 volts tension, with electrodes unattackable by acids. Without plentiful excess of current, *i.e.*, without a big production of hydrogen in the cathode chamber, and without the protection of the paraffin covering, the yield of *p*-aminothymol is small, but with the patentee's process it exceeds 60 per cent.

The aminothymol in solution, after neutralising the greater part of the solvent acid, is directly diazotised, and reduced to eliminate the amino-group, or poured into an excess of sodium bisulphite solution and precipitated as a base with caustic soda solution, or salted out after adding the caustic soda solution. After decantation the base is dissolved in hydrochloric acid. The solution is diazotised and the amino-group eliminated with stannous chloride in acid solution after its transformation into thymol-hydrazine, or the diazoic solution is poured into a concentrated caustic soda solution, strongly cooled, and reduced with an alkaline solution of stannite of sodium. After being left some



time alone, it is boiled, and finally acidulated in order to precipitate the thymol; this is steam distilled; the distillation product gives in a short time rose-coloured crystals of thymol.

Thymol thus obtained is dried and reduced with hydrogen and nickel as a catalyst, to menthol in an autoclave fitted with a stirrer. The best catalyst for this purpose is obtained if nickel is precipitated as nickel carbonate from a solution of nickel sulphate on kiesulguhr and heated to 350° to 400° in a current of hydrogen. The reduction with this catalyst may be effected at 160° to 170° at a pressure of 15 atmospheres, with brisk stirring, very little menthone only being produced as a by-product. The yield is 80 per cent. of the thymol, or even more; the residue is unattacked thymol, which may be washed out from the reaction product with dilute caustic alkali solution. The crude menthol is either oxidised in acetic acid solution with chromic acid to menthone, and this reduced in alcoholic solution with metallic sodium to inactive menthol, or it is transformed into the phthal-esteric acid salt and the *i*-menthol regenerated therefrom by saponification.

Spanish oil of pennyroyal is the most easily accessible, but the process can equally be used with the pennyroyal oils from North Africa or Asia Minor, or with the oils from *Hedeoma pulegioides*, *Pycnanthemum lanceolatum*, *Bystropogon origanifolius*, or *Calamentha nepeta*.

Smith and Penfold (*Jour. and Proc. Royal Soc. N.S.W.*, liv., 40) have shown that menthol can be prepared by the direct reduction of piperitone (*q.v.*), but is always accompanied by a considerable amount of a bimolecular ketone. If, however, piperitone be first reduced to menthone (*q.v.*), the latter is easily further reduced to menthol.

The menthone prepared from piperitone was treated with sodium in aqueous ether solution, repeatedly adding the metal in small quantity until the reduction was thought to be complete. The reduced product did not, however, solidify at room temperature, although it readily formed a solid mass when the vessel containing it was stood upon ice. As the melting point of menthol prepared in this way is only 34° C., it follows that a very small quantity of unreduced menthone would be sufficient to prevent crystallisation under atmospheric conditions. The menthol was therefore purified by the phthalic acid combination in the ordinary way, when a good return of crystallised menthol was obtained. It should not be difficult, however, to devise methods for the

## P E R F U M E R Y

preparation of crystallised menthol from the partly reduced menthone by freezing out and separating by mechanical means, similarly to those employed in the manufacture of cineol. Although it might be a difficult matter to economically prepare the optically active components from the inactive menthol thus produced, yet this has been accomplished in the laboratory, and Pickard and Littlebury (*Proc. Chem. Soc.*, 1912, 101, 111) have shown that, when thus separated, both the *dextro*- and *laevo*-menthols melted at 43° C.

Penfold (see *P. & E. O. R.*, 1924, 277) has just reported on a sample of menthol manufactured from piperitone as follows:—

“A commercial sample *ex* bulk stock of synthetic menthol manufactured from piperitone was examined, with the following results: It was a perfectly colourless viscous liquid, which readily solidified during cool weather at a temperature of 15° to 17° C. It produced an excellent cooling effect, and possessed a typical menthol odour and taste. It possessed the following constants:—

|   |             |
|---|-------------|
| Specific gravity $\frac{15^\circ}{15^\circ}$ C. | 0.9068      |
| Optical rotation                                | — 3.6°      |
| Refractive index, 20° C.                        | 1.4634      |
| Boiling point at 774 mm.                        | 212-213° C. |

“These constants are in agreement with those for chemically pure natural menthol, with, of course, the exception of rotation. The solidified oil melted at 23° to 24° C., and so, although usually in the liquid condition, would be a solid in a cold climate. On investigation it was found to consist of two isomers of the same boiling point, 212° to 213° C., but the solid inactive menthol of melting point 34° C. was found to preponderate. The liquid form was *laevorotatory*. So far as I am aware, it is the first record of a synthetic menthol having a *laevorotation*.”

Menthol forms an acetic ester, menthyl acetate  $C_{10}H_{19}O.COCH_3$ , a viscous, highly refractive liquid boiling at 224°, and a benzoic ester  $C_{10}H_{19}O.CO.C_6H_5$  melting at 54°. It also forms a phenyl urethane melting at 111° to 112°.

Boedtker (*Bull. Soc. Chim.*, 1915, iv., 17, 360) has prepared a number of the homologues of menthol. Sodamide was allowed to react with menthone in ethereal solution. The resulting sodium menthone was then treated with the various alkyl iodides, with the formation of the corresponding alkyl menthones. These were reduced with sodium, and thus yielded the corresponding menthol

## P E R F U M E R Y

homologues. The alkyl menthols so prepared had the following characters :—

|                 | Boiling point.      | Specific gravity at $\frac{18^{\circ}}{4^{\circ}}$ . | Specific rotation. | Refractive index. |
|-----------------|---------------------|--|--------------------|-------------------|
| Methyl menthol. | 130° at 22 mm.      | 0.912  | — 2° 26'           | 1.4692            |
| Ethyl menthol.  | 124° at 13 mm.      | 0.925  | + 4° 55'           | 1.4769            |
| Propyl menthol. | 141°–145° at 27 mm. | 0.907  | + 29° 7'           | 1.4675            |
| Isoamyl menthol | 150° at 23 mm.      | 0.898  | + 33° 44'          | 1.4661            |
| Benzyl menthol. | 203°–205° at 24 mm. | 0.983  | — 43° 19'          | 1.5957            |

Menthol is used for the same purposes as peppermint oil where the powerful menthol odour and flavour, free from those of the secondary constituents of the oil, are desired. Traces in eau de Cologne give it a very "cooling" effect on the skin.

**MENTHONE.**—Menthone is a ketone of the formula  $C_{10}H_{18}O$  found associated with menthol in peppermint oils. It is a liquid with a mint-like odour, having the following characters :—

|                            |                        |
|----------------------------|------------------------|
| Specific gravity . . . . . | 0.894                  |
| Refractive index . . . . . | 1.4495                 |
| Boiling point . . . . .    | 206°–208°              |
| Optical rotation . . . . . | About $\pm 26^{\circ}$ |

There are probably a number of isomeric menthones corresponding with the isomeric menthols. (*Vide* "Menthol.")

Menthone has been obtained synthetically by various methods (*Annalen*, 1905, **342**, 306 ; 1908, **362**, 261).

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Pure piperitone was subjected to the action of purified hydrogen in the presence of a nickel catalyst for six hours, the temperature ranging between 175° to 180°. The double bond in piperitone was readily opened out with the formation of menthone, but further action of the hydrogen under these conditions did not reduce the carbonyl group, even after continued treatment for two days. Under correct conditions, however, the reduction to menthol should take place. The ease with which menthone is formed in this way is of special interest, not only in connection with the production of this ketone, but also as a stage in the

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## P E R F U M E R Y

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manufacture of menthol. The reduction of piperitone to menthone cannot well be brought about by the action of sodium or of sodium-amalgam in alcoholic solution, because, with the latter particularly, a solid bimolecular ketone is formed at once. This is a finely crystallised substance, melts at  $148^{\circ}$  to  $149^{\circ}$ , and has the formula  $C_{20}H_{34}O_2$ . Piperitone thus follows the rule with substances having a conjugated double bond—carvone, for instance, which also forms a bimolecular ketone on reduction, melting at  $148^{\circ}$  to  $149^{\circ}$ . The menthone was prepared from piperitone in almost quantitative yield, and had the characteristic peppermint odour of this substance. It was colourless, boiled at  $208^{\circ}$ , had a specific gravity at  $20^{\circ} = 0.8978$ , optical rotation  $\alpha_D - 0.15^{\circ}$ , and refractive index at  $20^{\circ} = 1.4529$ . The oxime melted at  $80^{\circ}$ , the more soluble semi-carbazone at  $156^{\circ}$ , while the less soluble melted at  $187^{\circ}$  to  $188^{\circ}$ . Any unreduced piperitone can be removed from the menthone by the action of neutral sodium sulphite.

Good results were also obtained by electrolytic reduction, using platinum as the anode and activated nickel as the cathode, but the product was almost entirely isomenthone.

**MENTHYL ACETATE.**—Menthyl acetate,  $CH_3.CO.O.C_{10}H_{19}$ , is an ester occurring naturally in oil of peppermint. It is also formed by the esterification of menthol by means of acetic anhydride. It is an oil of peppermint-like odour, having the following characters :—

|                            |   |
|----------------------------|---|
| Specific gravity . . . . . | $0.925$ at $\frac{20^{\circ}}{0^{\circ}}$ |
| Boiling point . . . . .    | $228^{\circ}$                             |
| Optical rotation . . . . . | $- 73^{\circ}$                            |
| Refractive index . . . . . | $1.4468$                                  |

The relative proportions of free menthol and menthyl acetate in peppermint oils have a marked effect on their flavour and odour.

**MERIANDRA, OIL OF.**—The essential oil of *Meriandra benghalensis* has been distilled in Eritrea and examined by Schimmel & Co. (*Bericht*, October, 1911, 106). It has been termed "sage oil" locally. The oil has the following characters :—

|                            |                  |
|----------------------------|------------------|
| Specific gravity . . . . . | $0.951$          |
| Optical rotation . . . . . | $- 2^{\circ} 5'$ |
| Refractive index . . . . . | $1.4790$         |
| Acid value . . . . .       | $3.7$            |
| Ester value . . . . .      | $14.8$           |

The oil has a fragrant sage odour and contains camphor.

## P E R F U M E R Y

- MESPILODAPHNE, OIL OF.**—*Mespilodaphne pretiosa* (*Ocotea pretiosa*) is a Brazilian plant belonging to the natural order *Lauraceæ*. It is a native of Rio Janeiro and Minas Geraes, and is known locally as *Prisprisca*. The branches of the tree yield about 0.5 per cent. of a very fragrant essential oil having a cinnamon odour. This oil has the following characters :—

|                                       |                |
|---------------------------------------|----------------|
| Specific gravity . . . . .            | 0.891          |
| Optical rotation . . . . .            | + 7° 20'       |
| Refractive index . . . . .            | 1.4690         |
| Esters, as linalyl acetate . . . . .  | 4.65 per cent. |
| • Total alcohols as linalol . . . . . | 51.8 „         |

Laloue (*Bull. Soc. Chim.*, 11, 602) distilled 25 kg. of the wood, from which he obtained 0.69 per cent. of oil. This oil had an odour recalling that of rosewood and cinnamic alcohol. It separated during distillation into a heavy and a light oil. The benzoic acid esters of geraniol and linalol were found to be present.

*Schimmel & Co.* have examined the oil distilled from the bark (*Report*, April, 1913, 76), and found it to have a specific gravity 1.1200, and refractive index 1.5271. It contains the sesquiterpene caryophyllene and 65 per cent. of bodies soluble in solution of caustic alkali, which consists either of phenols or lactones or a mixture of these bodies.

**METHOXY-ACETOPHENONE.**—This body is anisyl-methyl ketone, having a fine floral odour. Its hydroxy derivative  $C_9H_{10}O_3$  is pænonol, an odorous compound occurring in some of the xanthorrhoea oils (*q.v.*), and which has been synthesised by Hoesch (*Berichte*, 1915, 48, 1122).

**METHOXY-BENZOIC ACID.**—This body, also known as anisic acid, has the constitution  $C_6H_4.OCH_3.CO_2H$ . It is found in aniseed oil and in Tahiti vanilla beans. It is a crystalline compound melting at 184°. It forms aromatic esters, such as methyl anisate (*q.v.*), which are of value in perfumery.

**METHOXY-CINNAMIC ALDEHYDE.**—This body, which is also known as *ortho*-coumaric-aldehyde methyl ether, has the constitution  $C_6H_4(CO.CH_3)(C.CH:CH.CHO)$ . It is present to a very small extent in cassia oil, from which it separates as a crystalline substance melting at 45° to 46°, and boiling at about 295°. The isomeric *para* compound is present in oil of tarragon, and is a liquid boiling at 170° at 14 mm. The latter compound also occurs in the essential oil of the root of a variety of chlorocodon

## PERFUMERY

(Goulding and Pelly, *Proc. Chem. Soc.*, 1908, 24, 62; Friedlander, *Monatshefte*, 1909, 30, 879).

**METHOXY-PHENYL ACETONE.**—This body is also known as anise ketone. It is a liquid, of the formula  $C_{10}H_{12}O_2$ , of specific gravity 1.095 at 0°, and boiling at 263°. It yields an oxime melting at 72°. It occurs in oil of fennel. It has an odour recalling that of aniseed.

**METHYL-ACETOPHENONE.**—*Para*-methyl-acetophenone is a ketone of powerful floral odour, also described as methyl-*para*-tolyl ketone. Its formula is  $CH_3.C_6H_4.CO.CH_3$ . It is manufactured by adding acetyl chloride to a suspension of powdered aluminium chloride in perfectly dry toluene. The addition must be gradual, the temperature must be kept low, and the liquid must be well agitated during the operation. When no more hydrochloric acid gas is evolved, the reaction mass is poured on ice water containing a little hydrochloric acid, the oily layer separated, washed first with water, then with dilute caustic, and dried and rectified. The product is a colourless liquid of specific gravity 1.0062, boiling at 220°, or at 128° at 22 mm. pressure. Its odour is very fragrant, and it is used as the basis of artificial mimosa perfumes, and also in cassie bouquets.

**METHYL-AMYL-CARBINOL.**—See “Heptyl Alcohol.”

**METHYL-AMYL-KETONE.**—This ketone has the formula  $CH_3.CO(CH_2)_4.CH_3$ . It has been isolated from the oils of cinnamon bark and cloves. It has a specific gravity 0.826, and boils at 151° to 152°. It forms a semicarbazone melting at 123°.

**METHYL ANISATE.**—Methyl alcohol forms an ester with anisic acid, of the formula  $C_6H_4(OCH_3)(COOCH_3)$ . It forms well-defined crystals melting at 44° to 45°, and having a fine chervil odour. It recalls the aromatic herb *Anthriscus cerefolium*. It is used in artificial flower perfumes, especially in conjunction with anisic aldehyde in hawthorn odours.

**METHYL ANTHRANILATE.**—See “Anthranilic Acid Esters.”

**METHYL BENZOATE.**—This synthetic product is also known as oil of Niobe. It is a highly fragrant ester, occurring naturally in the oils of tuberose, ylang-ylang, and other flower oils. It has a specific gravity 1.1026, refractive index 1.5170, and boils at 199°. It is prepared by passing a current of dry hydrochloric acid gas into a solution of benzoic acid in methyl



alcohol, or by heating equal parts of sulphuric acid, benzoic acid, and methyl alcohol under a reflux condenser for two hours. Its formula is  $C_6H_5COO.CH_3$ . It is a favourite constituent of perfumes of the *Peau d'Espagne* type, and is present in artificial ylang-ylang and similar oils.

**METHYL CAPRINATE.**—This ester,  $CH_3(CH_2)_8COOCH_3$ , is one of the most recent synthetic perfumes, being very expensive and very powerful. It has a fruity odour, and may be used in very minute amounts for giving a special note to flower bouquets. On saponification it yields capric acid, melting at  $31^\circ$  to  $32^\circ$ .

**METHYL CAPRYLATE.**—This ester,  $CH_3(CH_2)_6COOCH_3$ , is similar in characters to methyl caprylate. On saponification it yields caprylic acid, melting at  $16^\circ$  to  $17^\circ$ .

**METHYL-CHAVICOL.**—See "Estragol."

**METHYL CINNAMATE.**—Methyl cinnamate is found naturally in various balsamic products. Its composition is  $C_6H_5.CH:CH.COOCCH_3$ . It is a crystalline substance having the following characters:—

|  |                         |
|--|-------------------------|
| Specific gravity at $40^\circ$ . . . . | 1.0663                  |
| Refractive index at $35^\circ$ . . . . | 1.5682                  |
| Melting point . . . . .                | $34^\circ$ – $35^\circ$ |
| Boiling point . . . . .                | $256^\circ$ at 745 mm.  |

It is prepared by the condensation of methyl alcohol with cinnamic acid in the presence of hydrochloric acid. It has a sweet fruity odour, which to some extent recalls that of the strawberry, and has also very strong fixative properties.

**METHYL-COUMARIN.**—Bailey and Boettner (*vide P. & E. O. R.*, 1921, 407) have shown that methyl-coumarin can be obtained in a yield of 50 per cent. calculated on the malic acid, by the interaction of *meta*-cresol and malic acid in the presence of sulphuric acid. It has almost the same perfume value as coumarin (*q.v.*) and is less toxic.

**METHYL-DECINE CARBONATE.**—This body is a synthetic having a somewhat "waxy" floral odour, and is useful in the compounding of many floral perfumes. (See under "Hep-tine Carbonates.")

**METHYL-DUODECYL ALDEHYDE.**—This aldehyde is one of the recent additions to the modern synthetic perfumes, and is of an intense floral and fruity odour. It is a liquid, of the for-

## P E R F U M E R Y

mula  $C_{13}H_{26}O$ , boiling at  $112^{\circ}$  to  $113^{\circ}$  at 12 mm. It is prepared by the condensation of nonyl-methyl ketone with bromacetic ester in benzene solution in the presence of zinc. The condensation is carried out as in the case of methyl-nonyl aldehyde (*q.v.*), the quantities necessary being as follows: 1.54 kg. of nonyl-methyl ketone; 1.67 kg. of bromacetic ester; 1 kg. of zinc activated with copper; and 2 kg. of benzene. (See Lewinsohn, *P. & E. O. R.*, 1924, 79).

**METHYL-EUGENOL.**—This ether of eugenol, of the formula  $C_{11}H_{14}O_2$ , is found naturally in the essential oils of citronella, Japanese calamus, betel nut, bay, and numerous other essential oils. It is also prepared artificially by the action of methyl iodide on eugenol sodium. It possesses a very delicate odour, resembling that of eugenol, and is a useful adjunct to perfumes of the carnation type. Its characters are as follows:—

|                            |                 |
|----------------------------|-----------------|
| Specific gravity . . . . . | 1.040–1.043     |
| Refractive index . . . . . | 1.5340–1.5395 • |
| Boiling point . . . . .    | $248^{\circ}$   |
| Optical rotation . . . . . | $0^{\circ}$     |

It is characterised by the formation of veratric acid  $C_6H_3(COOH)(OCH_3)_2$ , melting at  $179^{\circ}$  to  $180^{\circ}$ , when 6 grams of methyl eugenol are oxidised with a solution of 18 grams of potassium permanganate in 400 c.c. of water.

**METHYL-HEPTENOL.**—This body is an alcohol occurring in both Cayenne and Mexican linaloe oils. It is an oil of delicate rose odour, of the formula  $C_8H_{16}O$ . It is prepared artificially by the reduction of methyl-heptenone. It has a specific gravity 0.858; optical rotation,  $-1^{\circ} 34'$ ; refractive index, 1.4495; and boiling point,  $179^{\circ}$  to  $180^{\circ}$ .

An alcohol of the same formula, which is identical or isomeric with the above, results from the interaction of aceto-butanol and ethyl magnesium iodide. It boils at  $92^{\circ}$  to  $94^{\circ}$  at 15 mm., and has a rose-geranium odour. Its acetate has a similar odour (Bogert and Slocum, *American Perfumer, etc.*, xviii., 12, 621).

**METHYL-HEPTENONE.**—This ketone,  $C_8H_{14}O$ , is found in lemongrass and other essential oils. It is a liquid of specific gravity 0.855 to 0.865, according to its source; refractive index about 1.438; and boiling point about  $173^{\circ}$  to  $175^{\circ}$ . Its odour is fruity, recalling isobutyl and amyl acetates. It forms a semi-carbazone melting at  $137^{\circ}$  to  $138^{\circ}$ . It is obtained as a by-

product in ionone manufacture, and is used to some extent in soap perfumery.

**METHYL-HEPTINE CARBONATE.**—See “Heptine Carbonates.”

**METHYL HEPTOATE.**—This ester is one of the more recent additions to the list of artificial perfumes. It has the formula  $\text{CH}_3(\text{CH}_2)_5\text{COOCH}_3$ . It has a powerful fruity odour, and may be used in very small amount in floral bouquets. On hydrolysis it yields a liquid fatty acid.

**METHYL-HEPTYLENE CARBINOL.**—This body, of the formula  $\text{C}_9\text{H}_{18}\text{O}$ , results from the reduction of methyl-heptylene ketone by means of sodium and alcohol. It is an oil with a delicate rose odour, and has a specific gravity 0.8515; optical rotation,  $0^\circ$ ; refractive index, 1.4458; and boiling point,  $186^\circ$  to  $187^\circ$ .

**METHYL HEPTYL KETONE.**—This ketone,  $\text{CH}_3\text{CO}(\text{CH}_2)_6\text{CH}_3$ , has been found in otto of rose and in oil of cloves. It has a specific gravity 0.835, and boils at  $196^\circ$ . It yields a semi-carbazone melting at  $119^\circ$ .

**METHYL-HEXANONE.**—This ketonic compound,  $\text{C}_7\text{H}_{12}\text{O}$ , is a natural constituent of pennyroyal oil. It is a highly aromatic liquid, having the following characters:—

|                  |       |                                     |
|------------------|-------|-------------------------------------|
| Specific gravity | . . . | 0.911 at $\frac{18^\circ}{4^\circ}$ |
| Boiling point    | . . . | $167\text{--}168^\circ$             |
| Optical rotation | . . . | $+11^\circ 21'$                     |

**METHYL-INDOL.**—See “Skatol.”

**METHYL-IONONE.**—See “Ionone.”

**METHYL-ISOEUGENOL.**—This body, of the formula  $\text{C}_{11}\text{H}_{14}\text{O}_2$ , bears the same relationship to methyl-eugenol as isoeugenol does to eugenol. It is found naturally in the essential oil of *Asarum arifolium*, and is obtained artificially by the action of methyl iodide on isoeugenol sodium, or by isomerising methyl eugenol by means of hot alcoholic potash. It is an oil of carnation-like odour, having a specific gravity 1.062; refractive index 1.5720; and boiling point,  $263^\circ$ . On oxidation it yields veratric acid, melting at  $179^\circ$  to  $180^\circ$ .

**METHYL ISOVALERIANATE.**—This ester,  $\text{C}_4\text{H}_9\text{COO} \cdot \text{C}_{10}\text{H}_{19}$ , is found in American oil of peppermint. It can be prepared

## P E R F U M E R Y

artificially by heating menthol with isovalerianic acid and sodium acetate. It is a fragrant oil, having the following characters:—

|                            |             |
|----------------------------|-------------|
| Specific gravity . . . . . | 0.907–0.908 |
| Optical rotation . . . . . | — 56° 30'   |
| Refractive index . . . . . | 1.4486      |

**METHYL LAURINATE.**—This ester, of the formula  $\text{CH}_3(\text{CH}_2)_{10}.\text{COOCH}_3$ , is one of the powerful fatty acid esters, used in the same manner as, for example, methyl heptoate (*q.v.*). On hydrolysis it yields laurinic acid, melting at 43° to 44°.

**METHYL MALONATE.**—This substance is prepared by treating potassium cyanacetate with methyl alcohol and hydrochloric acid. It is a liquid of the formula  $\text{CH}_2(\text{COOCH}_3)_2$ , boiling at 181°. On hydrolysis it yields malonic acid, melting at 132°. It has a powerful fruity odour, and is used in the same way as the esters of the normal fatty acids, such as methyl heptoate (*q.v.*). If more than mere traces of these “fruity” esters be used in the preparation of floral bouquets, the odour, instead of having a fine special “note” of its own, becomes repulsive.

**METHYL METHYLANTHRANILATE.**—This body is very similar in odour to methyl anthranilate. Its constitution is  $\text{C}_6\text{H}_4(\text{NH}.\text{CH}_3)(\text{CO}.\text{OCH}_3)$ . It is a highly odorous substance, with a powerful fluorescence. Its odour resembles that of neroli oil. It is a crystalline substance, melting at 18.5° to 19.5°; of specific gravity 1.1238 at 20°; and refractive index, 1.5796. It is useful in compounding artificial oil of neroli.

**METHYL NAPHTHYL KETONE.**—There are several methyl naphthyl ketones known, of which that denominated acetone naphthone  $\text{C}_{10}\text{H}_7.\text{CO}.\text{CH}_3$  is formed by the condensation of naphthalene and acetyl chloride in the presence of aluminium chloride. This body melts at 34° and boils at 295°. It is a white crystalline powder, having an odour of orange blossom, and is a useful ingredient and fixative in eau de Cologne. (See also ‘Acetone naphthone.’)

**METHYL-NONENE-OL.**—This alcohol results from the interaction of acetobutanol and *n*-butyl magnesium iodide. It boils at 109° to 111° at 11 mm., and has a fine floral odour (Bogert and Slocum, *American Perfumer, etc.*, xviii., 12, 621).

**METHYL-NONYL ALDEHYDE.**—There are two ten-carbon fatty aldehydes used by perfumers of the formula  $\text{C}_{10}\text{H}_{20}\text{O}$ . Of these, one is normal decyl aldehyde (*q.v.*), and the other is *b*-methyl-nonyl aldehyde. The latter substance is similar in characters to other members of the higher fatty aldehyde series

(see "Aldehydes, Higher Fatty"), and with its intense floral-fruity odour requires great care and restraint in its use, as more than traces will ruin any composition into which it enters. It is prepared by the condensation of bromacetic ethyl ester (ethyl bromacetate) with methyl hexyl ketone in the presence of zinc, with the further reactions as described below.

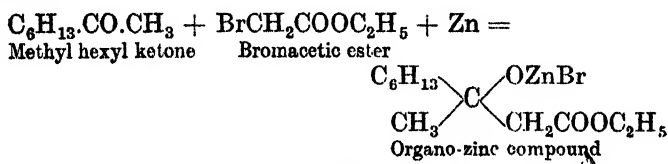
Ethyl bromacetate is prepared by heating glacial acetic acid with 5 per cent. of flowers of sulphur and, when the mixture is boiling, adding bromine gradually (2.4 kg. of bromine per kilogram of acetic acid), and esterifying the monobromacetic acid with absolute alcohol and a little sulphuric acid.

To perform the preliminary condensation, it is advantageous to render the granulated zinc to be used active, by means of a trace of copper electrolytically deposited thereon, by warming the zinc for a few minutes with a solution of copper sulphate. The bromacetic ester (5,840 grams) is mixed with methyl hexyl ketone (5,000 grams) and benzene (7,000 grams). The mixture is heated to 100° and the zinc added in portions of about 200 grams until 3,000 grams have been added, great care being observed that the temperature is well regulated, or the reaction will take place with great violence. After all the zinc has dissolved, the mixture is heated for a further half hour, and then poured on to ice water and acidified with hydrochloric acid. The product of the reaction is in the benzene layer, which is separated and well washed with water and with dilute sodium carbonate solution, dried over sodium sulphate, and rectified *in vacuo*. The fractions should be collected as follows (Lewinsohn, *P. & E. O. R.*, 1924, 44):—

- (1) Below 110° at 12 mm. (benzene and unaltered ketone).
- (2) 111° to 125° at 12 mm. (mixture of hydroxy ester and unsaturated ester).
- (3) 126° to 145° at 12 mm. (hydroxy ester).
- (4) 146° to 160° at 12 mm. (over-condensed product).

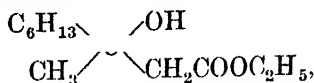
Fractions (2) and (3) are refractionated, and yield about 300 grams of unsaturated ester and about 4,100 grams of the desired hydroxy ester.

The hydroxy ester is formed according to the following reactions:—



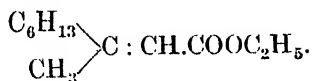
## P E R F U M E R Y

This organo-zinc compound reacts with a molecule of water and becomes the necessary hydroxy ester

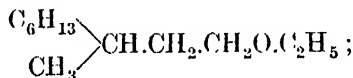


zinc oxide and hydrobromic acid being formed.

This ester is now dehydrated, by, for example, passing its vapours over aluminium oxide heated to 340° in an earthenware tube. Water is evolved and *b*-methyl-*b*-hexyl-acrylic ethyl ester is formed, of the formula



This is reduced, and results in the ethyl ester of methyl-nonyl alcohol



and the free alcohol, deprived of 2 atoms of hydrogen, becomes methyl-nonyl aldehyde



It is a powerfully aromatic liquid, boiling at 99° to 100° at 12 mm.

**METHYL NONYLATE.**—This ester,  $(\text{CH}_3(\text{CH}_2)_7\text{COOCH}_3$ , is one of the powerful fatty acid esters, of strong fruity odour, used in the same manner as methyl heptoate (*q.v.*). On hydrolysis it yields nonylic acid melting at 12 to 13°.

**METHYL-OCTINE CARBONATE.**—This body has a fine violet-leaf odour, and is of considerable value in artificial violet bouquets. (See "Heptene Carbonates.") It has a specific gravity about 0.923, and boils at 122° at 19 mm.

**METHYL *para*-TOLYL KETONE.**—See "Methyl-acetophenone."

**METHYL PHENYLACETATE.**—This ester is a most valuable synthetic perfume. Like its parent acid, phenylacetic acid, it has a sweet, honey-like odour with a suggestion of musk. It is the basis of many of the perfumes bearing the name "Eglantine." The ester, of the formula  $\text{C}_6\text{H}_5.\text{CH}_2.\text{COOCH}_3$ , is prepared either by the direct esterification of phenylacetic acid or by the direct

## P E R F U M E R Y

esterification of benzyl cyanide. If the former process be used, the following details should be observed. One part of phenylacetic acid and 1 part of absolutely anhydrous methyl alcohol and 15 to 20 per cent. of concentrated sulphuric acid are heated under a reflux condenser for twelve hours. The liquid is decanted, washed with water, then with solution of sodium carbonate, and finally rectified *in vacuo*. Or 1 part of benzyl cyanide, 1 part of methyl alcohol, and 0.5 part of concentrated sulphuric acid are heated under a reflux condenser for forty-eight hours. Sulphate of ammonia is deposited, and the ester is purified by distillation *in vacuo*. It has a specific gravity 1.070, refractive index 1.5060 to 1.5070, and boils at 220°. Ethyl phenylacetate (*q.v.*) is very similar in odour, and is prepared in the same manner. Its specific gravity is 1.0368; refractive index, 1.499; and boiling point, 228°. Butyl phenylacetate is also prepared in a similar manner. Its odour is very fine, and it is in most of the perfumes bearing the name "Ideal." It has a specific gravity 0.997; refractive index, 1.4890; and boiling point, 260°.

**METHYL PHENYLPROPIONATE.**—Phenylpropionic or hydrocinnamic acid forms a methyl ester,  $C_6H_5.CH_2.CH_2.COOCH_3$ , when cinnamic acid is reduced by sodium amalgam, and the resulting acid is esterified with methyl alcohol in the presence of a diluted mineral acid. The ester is an oil of sweet odour, resembling that of the phenylacetic esters. It is very useful in floral bouquets.

**METHYL PHTHALATE.**—This ester has no legitimate use in perfumery, but is sometimes used as an adulterant. It is what is known as an "artificial ester" in oils which contain naturally occurring esters. (See "Esters, Artificial.")

**METHYL SALICYLATE.**—This ester is practically identical with the natural essential oils of wintergreen and sweet birch. It is usually known as artificial oil of wintergreen. It is prepared by the condensation of methyl alcohol with salicylic acid in the presence of a little sulphuric acid. This ester,  $C_6H_4(OH)(COOCH_3)$ , is a highly refractive liquid having the following characters.—

|                  |   |   |   |   |        |
|------------------|---|---|---|---|--------|
| Specific gravity | . | . | . | . | 1.1815 |
| Boiling point    | . | . | . | . | 224°   |
| Melting point    | . | . | . | . | — 9°   |
| Refractive index | . | . | . | . | 1.5375 |

On hydrolysis it yields pure salicylic acid. It is used to a

## PERFUMERY

considerable extent as a perfume flavour for tooth pastes and washes, and for flavouring certain types of chewing gum. In small quantities it is useful to modify the odour of flower bouquets. Ethyl salicylate (*q.v.*) is very similar in all its properties.

**METHYL VALUES OF ESSENTIAL OILS.**—The amount of the methyl radicle  $\text{CH}_3$  present in essential oils is very variable, and its determination is sometimes useful. The methyl value is understood to be the amount of "methyl"  $\text{CH}_3$  expressed in milligrams obtained from 1 gram of the oil. The determination is carried out as follows:—

From 0.2 to 0.3 gram of the oil is heated on a glycerine bath with 10 c.c. of pure hydriodic acid (specific gravity, 1.7) in a flask having a capacity of 30 to 35 c.c., at the same time a current of carbon dioxide being passed through the mixture. The alcoholic iodide is made to bubble successively through water and water containing red phosphorus in suspension, the tube being maintained at a temperature of  $70^\circ$ , and finally led into a flask containing 5 c.c. of silver nitrate solution (40 per cent.) and 50 c.c. of alcohol (95 per cent.). The carbon dioxide, before escaping from the apparatus, passes through a separate flask containing 1 c.c. of silver nitrate solution and 10 c.c. of alcohol. After two hours the argentic solutions are mixed, decanted, and the precipitate is washed three or four times by decantation with 25 to 30 c.c. of water. Sufficient water is added to the liquid to produce 300 c.c., 10 drops of nitric acid are added, and the mixture is heated on a boiling water bath to remove the alcohol, the amount being then completed to 300 c.c. by the addition of boiling water. The first precipitate is heated with 20 c.c. of nitric acid, followed by decantation, whereupon both precipitates are collected on a tared double filter, washed, and dried at  $120^\circ\text{C}$ . The weight of the residue, multiplied by 15 and divided by 235, indicates the amount of methyl represented by the precipitate of silver iodide calculated for 1 gram of oil.

**MIGNONETTE.** The popular flower known as mignonette (*Fr. little darling*) is *Reseda odorata*, one of some twenty or more species of *reseda* belonging to the natural order *Resedaceæ*. It is said to have been introduced into England about the middle of the eighteenth century, and in 1752 was being cultivated in the Botanic Gardens at Chelsea. The plant is cultivated on a fair scale in the south of France, where its flowers attain a much finer fragrance than do those grown in England. The flowers are treated



## PERFUMERY

with volatile solvents, and are also subjected to the enfleurage process. The essential oil, which is only obtained to the extent of about 0.002 per cent., has been prepared by *Schimmel & Co.* (*Report*, October, 1893). It is a semisolid substance of intense floral odour, but is rarely met with in commerce. The oil obtained by distillation of the petroleum extract of the flowers has been examined by von Soden and found to have a specific gravity 0.961; optical rotation,  $+31^{\circ} 20'$ ; acid value, 16; and ester value, 85. *Messrs. Schimmel & Co.* also obtained 0.035 per cent. of essential oil from the fresh root of the mignonette plant. This root oil has an unpleasant odour, recalling that of radishes. It contains phenyl-ethyl thiocarbimide. Its specific gravity is about 1.085, and optical rotation  $+1^{\circ} 30'$ .

Most of the reseda perfumes sold to the public are mixtures of natural mignonette with artificial perfumes. There are no artificial perfumes having an odour really resembling reseda, so that such mixtures are really the true reseda perfume "improved"—or modified—by synthetics. Ethyl-decyl carbonate (*q.v.*) is one of the most characteristic of these, and there are also used homologues of phenyl-ethyl alcohol, methyl hexyl ketone, and traces of duodecyl aldehyde. Numerous formulæ are to be found in the usual books on practical perfumery, but in all cases the greatest care should be taken to use these powerful synthetics with restraint, usually in far smaller quantities than recommended, or the very delicate reseda perfume will be turned into a vulgar and objectionable substance. Reseda geraniol, obtained by distilling geraniol over the flowers, is a commercial article.

**MIMOSA.**—See "Acacia."

**MINT OILS.**—There are several species of *Mentha* other than those from which the peppermint oils of commerce are produced. The latter oils will be found described under "peppermint" oils. The chief of the other mint oils is that known as "spearmint." The essential oil known under this name is distilled from plants of different botanical origin, according to the country of distillation. The plant generally used for the distillation of spearmint oil in Great Britain and the United States is *Mentha viridis* L. (*Mentha spicata*), of which several varieties exist. In northern America the principal variety distilled is *M. spicata* var. *tenuis*, whilst in England it is *M. spicata* var. *trichoura*. In Germany, *M. crispa* and *M. longifolia* var. *undulata* are the principal plants distilled. A Russian spearmint is *M. verticillata* var. *strabala*, and probably *M. verticillata* var. *ovalifolia*.

## PERFUMERY

E. M. Holmes (*P. & E. O. R.*, 1911, 197) gives the following account of the plant :—

“The oil of spearmint of commerce appears to be chiefly produced in the States of New York and Michigan, in North America, from a plant which has been identified as *Mentha viridis*. L. There is, however, the probability that the same species or variety is not always employed, since there are two plants cultivated in gardens in this country under the name of spearmint or garden mint.

“An oil distilled by Messrs. Fritsche Bros., from a spearmint cultivated in their factory ground at Garfield, in New Jersey, was stated by them to have an odour quite different from that of the commercial oil, recalling that of carvone, and having a specific gravity of 0.980, that of *Mentha viridis* being 0.920 to 0.940. This difference *might* be due to the time at which the oil was distilled (*i.e.*, when the plant was in flower, in July), but it is not certain that this was the case, although an oil distilled from the same plant in October had a less delicate odour and its specific gravity and rotatory power were lower.

“The plant used in Germany to produce spearmint oil (known as *Krauseminze* or curled mint oil) is *Mentha crispa*, which is now regarded as a variety of *Mentha aquatica*. This mint is chiefly cultivated as a herb for medicinal purposes, and the oil is prepared in comparatively small quantity from the waste obtained in drying the herb for the market. The difference between the German and American oil is not sufficient to be distinctive, and the oils are considered to be practically identical (Parry).

“The oil distilled in this country, which is more expensive than the others, is stated to be prepared from *Mentha viridis*.

“A Russian oil of spearmint, which has occasionally been offered, is believed to be distilled from *Mentha aquatica*, its specific gravity being 0.880 to 0.890, which is that of *M. aquatica*. It differs from spearmint oil in odour and contains only 5 to 10 per cent. of carvone, as against 56 per cent. (35 to 45 per cent.—Parry) in ordinary spearmint oil, but it contains 50 to 60 per cent. of *l*-linalol. This oil is said to be distilled in Russia in large quantities, but chiefly for home consumption.

“The odours of mints are quite as variable as those of the roses, but more difficult to describe, and the plants themselves vary much in odour in different varieties of the same species, and the same or a very similar odour may occur in different species. The species in which the spearmint odour occurs, more or less modified,

but still recognisable, are *Mentha sylvestris* and its varieties *pemorosa* and *mollissima*, and *longifolia*, *M. alopecuroides*, *M. cardiaca*, *M. aquatica* var. *crispa*, Benth., and *M. javanica*, Benth., which is probably a form of *M. arvensis*, and some forms of *Mentha Canadensis*.

"Mint has been used from the earliest times. The mint mentioned in the Scriptures is believed to be *Mentha sylvestris*, which is still extensively cultivated in the East, and this is probably the plant which was chiefly used by the Romans, since it is called in the time of Gerarde (A.D. 1633) *Mentha Romana* and *Mentha Saraceniæ*. It is remarkable that, whilst Gerarde also calls it spearmint, he describes it as having hairy leaves, whilst the spearmint of the present day, *Mentha viridis*, has glabrous leaves; and Dodoens, who wrote still earlier (1616), also describes it under the same names and as 'right' garden mint, and states that the leaves are long, narrow, white, soft and hairy, almost like willow leaves, but larger, and the illustration he gives corresponds well with the form of *Mentha sylvestris* called *longifolia*, in the shape of the leaves and in the dense cylindrical flower spikes. Quite recently I have observed the hairy *Mentha longifolia* growing abundantly in a meadow near Dawlish, in Devonshire, intermixed with the smooth-leaved garden mint, *M. viridis*, both apparently quite wild. Indeed, it is probable that *M. longifolia* is the older form, and that *M. viridis* is derived from it.

"When the present glabrous or hairless form known as *Mentha viridis* came into use is not clear, but Sir John Hill, in his 'Herbal' (1716), says that it is a native of Germany, and not of this country, so that it may have been introduced into England about that date.

"Several, and at least four, species of garden mint were cultivated in the Middle Ages.

"In the 'Capitulary' of Charlemagne (A.D. 812) *Mentha*, *Menthastrum*, and *Sisymbrium* are mentioned, and these are respectively identified in Latin dictionaries as garden mint, wild mint, and water mint. In the writings of the Abbess Hildegarde in 1160, *Backmintze* (brook mint), *Mintze major*, *Rossmintze* (red mint), and *Romische mintze* are mentioned. It is difficult to determine which of the species now known to us were intended, but there is little doubt that the Roman mint was a form of *Mentha sylvestris*, the red or *rosmintze* was our *Mentha rubra*, *Mintze major* was probably *M. crispa*, and the *Backmintze* was probably *Mentha aquatica*. Fuchs in 1543 describes and figures a mint under the name of *Mentha hortensis*, or *Herz-kraut*, and

## P E R F U M E R Y

Morrison, in his 'Historia Oxoniensis' (A.D. 1699), figures the same plant under the name of *Mentha hortensis verticillata*, *Ocimi odore*. Parkinson includes the same plant with spearmint, under which name it was cultivated in gardens in his day. This plant is now known as *Mentha cardiaca*, and is still cultivated in gardens, as the true garden mint, especially in Wiltshire and Somersetshire, and in some parts of Kent.

"By the old herbalists it was considered inferior to *Mentha viridis* as a febrifuge, but as a stomachic and cardiac it was believed to be superior, whence its name. Judging from its odour it probably contains some other constituent than carvone, and the acetate of di-hydrocuminic alcohol, to which Elze has shown that the characteristic odour of spearmint is due (*Chem. Zeit.*, 1911, 1175). It would be interesting to ascertain what the constituent of the oil that modifies the spearmint odour may be, and whether it possesses any action as a heart stimulant. From its close resemblance in appearance and odour to ordinary spearmint, when not in flower, it is quite possible that the oil of this plant might at any time appear in commerce as that of spearmint, so that an examination of it is desirable. It is remarkable that, although the other mints formerly cultivated in gardens, e.g., *Mentha sylvestris*, *Mentha rubra*, and *Mentha rotundifolia* (which is probably the *Mentha crispa* of the old writers), are now found only in a wild state near villages, yet the *Mentha cardiaca* is still cultivated and replaces in many gardens the *Mentha viridis* of the Pharmacopœia."

Spearmint is distilled to a considerable extent in the United States, where it is known as "green mint." The American oil and the German oil (which is known as *Krausemin:oil*) are practically identical in characters, which are as follows -

|                  |       |                 |
|------------------|-------|-----------------|
| Specific gravity | . . . | 0.920-0.940     |
| Optical rotation | . . . | - 34° to - 52°  |
| Refractive index | . . . | 1.4820-1.4890   |
| Ester value      | . . . | 18-36           |
| Carvone content  | . . . | 38-65 per cent. |

Oils are occasionally found which do not comply with these limits. Schimmel & Co distilled an oil in Garfield, N.J., which had a specific gravity 0.980.

English spearmint oil does not differ greatly from the American oil, but is, perhaps, rather more delicate in odour.

Austrian oil differs from the above-described oils in containing as much as 60 to 72 per cent. of carvone.

# PERFUMERY

Russian oil is distinguished by a high percentage of linalol, and a low carvone content. It cannot be used in the ordinary way as spearmint oil, on account of its poor odour. Its characters are as follows :—

|                  |                |
|------------------|----------------|
| Specific gravity | 0.880–0.890    |
| Optical rotation | — 23° to — 27° |
| Carvone content  | 5–10 per cent. |
| Linalol content  | 50–60 „        |

According to Nelson, the American oil contains carvone, phellandrene, limonene, dihydrocarveol acetate, and esters of higher fatty acids.

Elze (*Chem. Zeit.*, 1910, 34, 1175) has examined a sample of German oil with interesting results. After removing the carvone, he found the oil to have a much more powerful spearmint odour. He identified dihydrocuminic acetate as the principal odour bearer of the oil, and when this body was saponified the spearmint odour disappeared.

|                    | Specific gravity. | Esters, per cent. | Total alcohols, per cent. |
|--------------------|-------------------|-------------------|---------------------------|
| 1908.              |                   |                   |                           |
| <i>Fresh herb.</i> |                   |                   |                           |
| Budding            | 0.925 at 22°      | 3.8               | 9.1                       |
| Flowering          | 0.929 „           | 4.6               | 8.5                       |
| Fruiting           | 0.929 „           | 8.7               | 13.4                      |
| 1909               |                   |                   |                           |
| <i>Fresh herb.</i> |                   |                   |                           |
| Budding            | 0.931 at 21°      | 8.6               | 12.0                      |
| Flowering          | 0.929 „           | 7.7               | 12.4                      |
| Fruiting           | 0.934 „           | 7.3               | 10.9                      |
| <i>Dried herb.</i> |                   |                   |                           |
| Budding            | 0.928 „           | 7.0               | 11.7                      |
| Flowering          | 0.933 „           | 10.8              | 12.7                      |
| Fruiting           | 0.925 „           | 9.1               | 15.6                      |
| 1910.              |                   |                   |                           |
| <i>Fresh herb.</i> |                   |                   |                           |
| Budding            | 0.931 at 23°      | 7.6               | 16.0                      |
| Flowering          | 0.925 „           | 13.4              | 18.4                      |
| Fruiting           | 0.930 „           | 15.9              | 21.4                      |
| <i>Dried herb.</i> |                   |                   |                           |
| Budding            | 0.912 „           | 10.8              | 15.7                      |
| Flowering          | —                 | 31.8              | 28.2                      |
| Fruiting           | 0.916 „           | 22.0              | 30.5                      |

## P E R F U M E R Y

Rabak (*Jour. Ind. Eng. Chem.*, 1918, 10, 4, 275) has carried out an investigation on the influence of external surroundings on the yield and character of the essential oil. He gives the characters shown in the table on p. 467 for the oils distilled from the materials described.

Water mint, *Mentha aquatica*, yields an oil having an odour of pennyroyal; and *Mentha sylvestris* yields a similar oil containing much pulegone and a little menthol. *Mentha pulegium* is the pennyroyal (*q.v.*).

**MIRBANE, OIL OF.**—Oil of mirbane, or nitrobenzene  $C_6H_5NO_2$ , is a very coarse almond perfume which is only used for very cheap perfumery work. Its odour is intense and somewhat irritating, and it is in no sense fit to replace the true almond oil or artificial benzaldehyde. It is a heavy oil, prepared by the direct nitration of benzene, having the following characters:—

|                   |           |        |   |
|-------------------|-----------|--------|---|
| Solidifying point | . . . . . | + 5°   | " |
| Boiling point     | . . . . . | 209°   |   |
| Specific gravity  | . . . . . | 1.2060 |   |
| Refractive index  | . . . . . | 1.5520 |   |

On reduction with iron filings and acetic acid, nitrobenzene yields aniline. For the detection of small quantities of mirbane oil, see "Nitro Compounds, Detection of"

**MOCK ORANGE.**—See "Syringa."

**MONARDA, OILS OF.**—A number of species of *Monarda* yield essential oils which are of interest to the perfumer. Of these the most fragrant is that distilled from *Monarda citriodora*, which is known in North America as the lemon mint. It is found in Illinois, westward to Nebraska and southward to Texas. The dry flowering herb yields about 1 per cent. of oil, which has been examined by Brandel (*Pharm. Rev.*, 1904, 22, 153). It is a reddish coloured liquid with an odour resembling that of lemon. Its specific gravity is 0.947 to 0.965. The principal constituent of the oil is the phenol carvacrol, which is present to the extent of 65 to 80 per cent. Traces of thymol are probably also present. Thymohydroquinone is present, and from 1 to 4 per cent. of citral, which accounts for the lemon-like odour. *Monarda didyma* yields a small amount of essential oil, which has also been investigated by Brandel (*Pharm. Rev.*, 1903, 21, 109). The previous statements in regard to this oil (*Arch. der Pharm.*, 1878, 212, 488) were probably based on the examination of the oil

## P E R F U M E R Y

from another species of *Monarda*, and neither thymol nor carvacrol was recorded as present in the oil. The following are Brandel's results :—

|                    | 1.     | 2.       | 3.       | 4.      | 5.       |
|--------------------|--------|----------|----------|---------|----------|
| Specific gravity . | 0.9055 | 0.8786   | 0.8855   | 0.8665  | 0.8740   |
| Rotation .         | —10°   | —24° 36' | —32° 38' | —7° 30' | —15° 45' |
| Refractive index . | —      | 1.4676   | 1.4689   | 1.4689  | 1.4674   |
| Ester value .      | —      | —        | 20.4     | 4.4     | 5.6      |

Sample No. 1 was distilled from the dry herb ; No. 2 from the half dried herb ; No. 3 from the nearly dry stems and leaves ; No. 4 and 5 from half wilted flowers.

The oil has a sweet balsamic odour, recalling that of lavender, with a suggestion of rosewood and amber.

*Monarda punctata*, the American horsemint, yields an essential oil having a strong thyme odour. It contains about 60 per cent. of thymol. *Monarda fistulosa* yields an oil rich in carvacrol.

**MONOACETIN.**—This ester, the monoacetic ester of glycerine, is used, either as such or as a constituent of impure "acetin" or "triacetin," as an adulterating artificial ester, in essential oils which contain natural esters. It has no legitimate use in perfumery. (See "Esters, Artificial.")

**MONODORA OILS.**—The seeds of *Monodora myristica* (called *Owere* seeds in West Africa), known also as the calabash nutmeg, yield about 6 per cent. of an essential oil which consists mainly of terpenes, but which has a lemon odour. Two samples examined at the Imperial Institute (*Bull. Imp. Inst.*, 1915, 13, 346) had the following characters :—

|                               | 1.     | 2.     |
|-------------------------------|--------|--------|
| Specific gravity . . . .      | 0.849  | 0.8592 |
| Optical rotation . . . .      | —44.7° | —57.8° |
| Acid value . . . . .          | 1.2    | 1.4    |
| Ester value . . . . .         | 1.9    | 6.4    |
| Ester value after acetylation | 52.9   | 33.5   |

The principal constituent is the terpene phellandrene.

The seeds of *Monodora grandiflora* yield a similar essential oil.

**MOSLA OILS.**—Several species of Mosla, plants growing in Japan, yield essential oils of a highly aromatic nature. *Mosla Japonica* yields about 2 per cent. of essential oil which contains either thymol or carvacrol. Some oils contain thymol, others

## P E R F U M E R Y

contain carvacrol, but apparently no oil contains both phenols. Hoshino (*Jour. Chem. Ind. Tokio*, 1919, 22, 557) gives the following as the characters of the oil :—

|                            |              |
|----------------------------|--------------|
| Specific gravity . . . . . | 0.9154       |
| Refractive index . . . . . | 1.4996       |
| Optical rotation . . . . . | + 1°         |
| Ester value . . . . .      | 4.5          |
| Thymol . . . . .           | 50 per cent. |

He identified phellandrene, cymene, terpinene, caryophyllene, cadinene, and probably sabinene.

*Mosla punctata* yields about 1 per cent. of oil of very fragrant odour, of specific gravity 0.897; optical rotation, — 9°; ester value, 16; and ester value after acetylation, 36.4. It contains a ketone which has been named mujone, and a sesquiterpene not yet characterised. The plant known as Himeshiso in Japan is *Mosla grosserata*. According to Furukawa and Tomizawa (*Jour. Chem. Ind. Tokio*, 1919, 22, 382), it yields 0.24 per cent. of essential oil containing carvacrol, thymoquinone, and thymohydroquinone. The oil from wild plants appears to differ considerably in composition from the oil from the cultivated plants.

**MOTIA GRASS.**—See “Geranium Oil.”

**MOUSSE DE CHÊNE.**—The oleoresinous matter extracted by means of volatile solvents from various lichens growing on oak and other trees is a fairly recent and highly valued raw material in perfumery. It is known as “oak moss resin” or “mousse de chêne,” and is a resinous material of the consistence of a thick syrup. Not only has it a characteristic “heavy” odour, which makes it of considerable value in the manufacture of heavy Oriental perfumes, but it has also a very high fixative value. The principal lichens used for its extraction are *Evernia furfuracea*, *Evernia prunastri*, and *Ramalina calicaris*. Various species of *Usnea*, *Alcetoria*, and *Parmelia* are also used for its manufacture. By steam distillation of the oleo-resin, Gattefossé has obtained a small amount of the essential oil, which has a very intense odour. According to Gattefossé, it consists principally of a crystalline phenol, melting at 72° to 73°, which he termed lichenol (*q.v.*). (See *La Parfumerie Moderne*, 1911, 4, 4; 1922, 227.) E. M. Holmes (*P. & E. O. R.*, 1913, 408) gives the following interesting account of lichen perfumes.

“The odorous principles of the lower, or leafless, cryptogamic plants offer an excellent field for investigation. Those who are familiar with the *Hepaticæ* cannot fail to notice the peculiar



bergamot scent of *Conocephalus conicus*, a common species on the shady banks of streams; those who know the seaweeds are only too familiar with the powerful and pungent odours given off by *Monospora pedicellata* and *Griffithsia corallina*. Lichenologists readily recognise the methyamine, or fishy odour, of *Stictina fuliginosa* and *S. sylvatica*, and the fungologist knows well the fragrant aniseed odour of *Hygrophorus agathosmus* and *Clitocybeodora* and the fætid odour of *Phallus impudicus*.

"For the purpose of retaining odours the common reindeer lichens *Cladonia rangiferina* and *C. sylvatica* answer admirably, being whitish, clean, and easily dried, and abundant in open healthy places where the soil is moderately damp.

"The use of the tree lichen *Evernia prunastri* as a basis for perfumes has been known for some years, the lichen being sold in France under the name of *Mousse de Chêne*, or oak moss:

"*Evernia prunastri* is one of the commonest lichens on trees and palings where the air is somewhat moist, and at one time was used by calico printers in this country as a substitute for gum in dressing calico, on account of the mucilaginous or starchy matter that it yields. But it is considered to yield more fragrance when growing on oak than on other trees. It can be distinguished from most of the other lichens with which it grows intermixed, by its repeatedly forked flat front, with slightly recurved margins, giving it a channelled appearance underneath, and by the frond being grey on the outside and white on the under or channelled side, the other species being uniform in colour on both sides. A variety of it, with rooting tips, is found growing on low sandhills near the sea. The fruit, which forms small brown discs on the frond, is exceedingly rare, the plant being propagated by soredia, or powdery granules which become free and give rise to new plants. This lichen has a fragrance which would hardly be recognised by an ordinary observer; its odour is stated by M. Gattefossé to be due to a phenol isomeric with carvacrol, which he has named lichenol. It is soluble in a 3 per cent. solution of carbonate of soda or other weak alkaline solution.

"Another lichen which possesses a fragrance similar to that of *Evernia prunastri* is *Lobaria pulmonaria*, known in this country as "Oaklungs," but distinguished in France as *Mousse de la base du chêne*, from its growing in France more frequently near the base of the tree trunk, although in this country it covers chiefly the upper part of the trunk below the lowest branches. This is considered to yield a more fragrant product, but being usually

## P E R F U M E R Y

confined to sub-alpine woods is scarcer and more expensive. It is more generally used by herbalists for medicinal purposes, having a reputation as a pectoral, and for use in internal hæmorrhage and in jaundice.

"The other lichens which grow with *Evernia prunastri*, and are liable to be mixed with it, are several species of *Ramalina*, especially those having powdery soredia, such as *R. farinacea*, *R. fraxinea* and *R. pollinaria*, but all these have grey, not brown, fruit discs, and are of a uniform grey colour on both sides. One species of this genus, *R. calicaris*, has a channelled frond, caused by a median depression, but it is more rigid, and has not the white under surface of *Evernia prunastri*. Whether the lichens of the genus *Ramalina* yield any odorous body has not yet been definitely ascertained, but they are considered to have little, if any, so that at present their admixture with the *Evernia prunastri* is likely to depreciate its value. According to M. Gattefossé, if the *Evernia prunastri* is extracted by volatile solvents, the product is a thick and not very soluble substance, containing chlorophyll, and a resin which can be isolated by acetone. If this extract is distilled *in vacuo* a much more fragrant and colourless body is obtained, which may take a definite and permanent place amongst perfumes as a basis."

Although the use of these lichens in perfumery is apparently only of recent date, they have in fact been used from very remote times, and then fell into disuse. The use of various highly fragrant lichens in perfumes and cosmetics is mentioned in many works of the sixteenth century, and earlier. In the examination of the ancient Egyptian royal tombs baskets filled with *Evernia furfuracea* and *Evernia prunastri* have been found, and in the tomb of Deir-el-Bahari *Usnea plicata* was also found (*Bull. Inst. Egypt*, No. 3; Joret, "Les Plantes dans l'antiquité et au moyen âge," Paris, 1897, i., p. 172).

St. Pfau (*Berichte*, 1924, 57, 468) and Späth and Jeschki (*ibid.*, 471) give interesting details of the synthesis of methyl everninate which has been isolated (by St. Pfau) from the methyl alcohol extract of the lichen *Evernia prunastri*. It does not appear to exist as such in the lichen, but in the form of the free acid, which is esterified by the methyl alcohol. It melts at 67° to 68°, and yields on hydrolysis the free acid melting at 170° to 171°. The ester has a weak anise-like odour. It is identical with the so-called sparassol, obtained in sugar solutions fermented by pure cultures of *Sparassus rumosa*.

## P E R F U M E R Y

Lichenol is the corresponding ethyl ester. Walbaum and Rosenthal (*Berichte*, 1924, 57, 770) state that orcinol monomethyl ester is the odoriferous constituent of oak moss oil, and they have also isolated methyl- $\beta$ -orcinolcarboxylate.

**MUGUET.**—See “Lily.”

**MURRAYA KOENIGII, OIL OF.**—The fruits of *Murraya koenigii*, a plant belonging to the natural order *Aurantaceæ*, which is widely distributed in the mountainous districts of the Himalayas, Bengal, and Ceylon, yield about 0.75 per cent. of a yellow coloured essential oil having an odour strongly resembling that of neroli oil. This, according to Gerber (*Ann. de l'Institut Colonial de Marseille*, 6), has the following characters:—

|                                   |           |
|-----------------------------------|-----------|
| Specific gravity at 13° . . . . . | 0.872     |
| Refractive index . . . . .        | 1.4870    |
| Optical rotation . . . . .        | — 27° 24' |

**MUSK.**—Musk is probably one of the oldest and most esteemed of all the raw materials used by the perfumer. It has for ages past been held in high veneration by the Chinese, who also have attributed to it very wonderful therapeutic activity. One of the celebrated physicians, Pao-po-tse, advised it as a certain safeguard against snake bites. He stated that the musk deer fed on reptiles, and a small fragment of musk carried by the traveller effectively kept reptiles away on account of the odour. The native Chinese name for musk is *shay hiang*, signifying “the perfume of the deer.” Tavernier is one of the earliest Europeans making mention of musk, stating in his diary that he purchased 7,600 pods of it during his voyages.

Sieur Barbe, the author of “*Parfumeur françois*” (see Chapter X., p. 321), who had probably never seen the “*Voyages*” of Tavernier, informs us that musk is the blood of an animal living in warm countries which is captured and bled and the blood dried.

Musk was probably introduced into Europe by the Arabs. It is found in the list of presents sent to the Emperor of Rome by Saladin in 1189. In the tenth century Avicenna mentions it in his *Pharmacopœia* as a remedy for various diseases, and the well-known traveller Marco Polo speaks of musk as a common commodity in the East.

Musk is a dried secretion of the preputial follicle of *Moschus moschiferus*, a small deer found principally on the mountains of northern India and in central Asia, its habitat being within 9° and 170° longitude E. and 65° and 15° latitude N. It is

## PERFUMERY

also found to a smaller extent in northern Siberia and in the north-east of Cochin China. But it is principally in Mongolia, Thibet, Nepaul, Cashmire, Assam, and Surkutan in China that the animal is hunted, and to some extent in the neighbourhood of Lake Baikal. The animals are very wild, very rarely gregarious in their habits, but often found in pairs. They usually conceal themselves during the day and come out of hiding to feed at night, and again in the very early morning. Hunting the musk deer is a very difficult matter, and is sometimes undertaken as a sport by Anglo-Indians. The use of dogs is impracticable, as the deer are so agile as to easily outstrip any dog in mountainous country. They are frequently captured by building hedges or barriers across places where they are known to frequent, with openings at fixed distances in which traps are inserted. It is necessary to visit these traps frequently, as larger wild animals will devour the captured deer if they find them. The greedy native kills all the animals he captures, even where the amount of musk is very small, so that the deer are in danger of extermination, as their breeding power is feeble. The secreting gland is peculiar to the male animal. The secretion is contained in a small sac situated immediately in front of the preputial orifice. This sac is formed by the invagination of the skin, and produces on its inner surface a number of alveoli, in which the secretion is formed and from which it is discharged into the cavity of the sac. The sac opens by a small canal close to the preputial orifice. In the fresh state the musk secretion is a syrupy liquid of about the consistence of honey, red brownish in colour. After the animal is killed, the musk gradually solidifies and becomes black and granular, but somewhat greasy to the touch. The gland is not found in the very young animal except in a rudimentary stage. The musk secretion has some relationship to the sexual affinities, as it is much more considerable when the female deer is in season, and also does not occur until the male is of adult age, and ceases when he has passed a certain age. It can be expelled from the sac by muscular contraction, and even without this occurring the air for a considerable space round the animal is permeated with the musk odour, and even the excrement of the animal smells strongly of musk, a fact which assists the hunter materially in picking up the trail.

The musk deer, being killed so promiscuously, is becoming scarce, and in order to prevent the extinction of the animal an edict has been issued by the Lamas of Tsarung, in south-eastern

Thibet. According to Dr. Joseph Rock, an explorer for the National Geographic Society, U.S.A., the edict provides (*P. & E. O. R.*, September 1st, 1924, p. 326) that hunters caught killing musk deer will have their hands cut off and nailed on the temple doors. On this point of slaughtering the deer, Clements (*P. & E. O. R.*, September, 1919) raised an interesting question, viz., "Could not some method be found to extract the musk secreted by the deer without destroying its life?" The number of deer killed to supply the market every year has been enormous. Only the male yields musk, and deer aged three to seven years, which bear small and medium sized pods, are the hunters' objective. Deer above seven years are scarce, because forest life does not conduce to such longevity. Every now and again older deer are caught yielding pods of from 1 to 2 oz. In the ordinary way twenty-two pods go to make a catty, taking small and large together, and on the average one catty means the death of twenty-two male musk deer. But both male and female, young and old, are indiscriminately snared, and Mr. Clements urged that it is reasonable to conclude that for every catty supplied at least thirty deer are killed. Since the annual export from Tachienlu was in the region of 2,000 catties, it follows that to supply the Tachienlu trade alone there was a yearly slaughter of 60,000. And when the exports from other towns are added, such as Sungpan, Kwanhsien, Batang, and Aduntze, the exports from the Szechuan Tibetan border passed beyond 100,000 head. It seemed that reproduction might not keep pace with destruction, and the musk deer would be in danger of extermination. This, apparently, the Lamas of Tsarung have recognised. But there might have been another way than prohibition of killing for dealing with the situation. As Mr. Clements pointed out in his article of September, 1919, it seems quite feasible that the musk deer could be reared in semi-captivity, and suitable means employed to extract a small quantity of musk annually. The preputial sac containing the musk is accessible, and has a natural opening on the outside, through which the musk might be drawn without injury to the animal. Those familiar with the ways of the musk deer state that the habit of the males is to lie down in places exposed to strong sunshine and relax themselves, in which condition the sac opens by itself and the musk is exposed. This aspect of the matter might be further considered by those in Thibet and elsewhere interested in the maintenance of the deer and a supply of natural musk respectively.

## PERFUMERY

In commerce musk is usually sold in the pods, as they are called. A certain amount of so-called "grain musk" is sold, but as the temptation to adulterate so expensive a product is very great—and adulteration is frequently practised—most perfumers prefer to purchase it in the original condition and prepare it themselves. There is, however, a certain amount of adulteration practised with the pods themselves. The adulteration commences at the hands of the merchant who purchases the musk from the actual hunters, and who then has to transport it, sometimes for a thousand and more miles, to the ports. In his leisurely journey in the caravan the Chinese merchant will skilfully open the pods, insert such adulterants as dried blood, albumen, or earthy matter, and so cunningly close the pods that only an expert can detect that the pod has been interfered with at all. Musk brought into Shanghai was at one time subject to a heavy tax, which was usually paid in kind. If the merchant were so foolish as to offer adulterated pods in payment of the tax, the mandarin did not discuss the matter, but promptly ordered the dishonest merchant to be executed. Hence this "Government" musk was sought after as always being of the very finest quality. Musk is exported from China in small boxes covered with silk and lined with lead. These are known here as catties or caddies, the name really only signifying the weight of the musk (1 catty = 22 oz.). The amount of musk exported from China varies from about 1,000 to 3,000 catties per annum.

The principal varieties of musk are the following: (1) Nankin musk, (2) Tonkin musk, (3) Yun-nam musk, (4) Cabardine musk, (5) Nepaul musk, and (6) Assam musk.

Nankin musk is the finest musk procurable, but is scarcely a commercial article. It is, or was, never adulterated.

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## PERFUMERY

resembling steel, hence the appellation "blue skin." The preparation of this blue skin musk, which is much prized, is a very delicate operation, and is performed by specially trained Chinese, principally in Shanghai. According to C. C. Treatt, the advantages claimed for blue skin musk are the following: (1) The character of the musk can be more readily judged without the necessity of opening the pod; (2) there is less chance of adulteration, as the pod is too delicate to stand any rough handling; (3) the musk is easier to granulate; (4) there is less skin to go bad—a pod whose skin has commenced to putrefy may spoil the odour of a large parcel of musk with which it is in contact; (5) the beautiful appearance of blue skin musk appeals to users.

Yun-nam musk is really only a variety of Tonkin musk, and appears to be only distinguished locally, and not to any extent in the consuming markets. The pods are more pear-shaped than the Tonkin pods.

Cabardine musk is not of nearly so fine an odour as Tonkin musk, but, being less valued, is also less adulterated. It is gathered principally in Siberia, although a certain amount is collected in northern China. The pods are more oval, and flatter in shape, than those of the Tonkin musk. They are also more hairy, and are frequently considerably more moist. In this condition the musk has sometimes not set completely, so that the pods contain a yellow liquid. In this condition they are known as "squeakers." The Russian cabardine musk was before the war exported *via* Petrograd, whilst the Chinese variety arrived in commerce through the same channels as the Tonkin musk.

Nepaul musk is only seen on the London market at very irregular intervals, most of it being used in the East. The pods are very small, about one-third of the size of Tonkin musk pods. They are in the form of hard, round balls, covered with hair about an inch long. The grain is quite dry, and on account of the care with which it is prepared it never has an odour of ammonia. Assam (or Bengal) musk is also only rarely obtainable, and then only in small quantities. The pods resemble the Nepaul pods, with the exception of their having a much darker skin. Grain musk is an elastic term, which *should* only mean the pure granulated contents of one or other type of genuine musk pods. It is a fact, however, that much of the "grain musk" of commerce is well reduced by various adulterants in the course of the granulation.

A pure dry musk should contain from 50 to 75 per cent. of matter soluble in water, but only about 10 to 15 per cent. of

## PERFUMERY.

In commerce musk is usually sold in the pods, as they are called. A certain amount of so-called "grain musk" is sold, but as the temptation to adulterate so expensive a product is very great—and adulteration is frequently practised—most perfumers prefer to purchase it in the original condition and prepare it themselves. There is, however, a certain amount of adulteration practised with the pods themselves. The adulteration commences at the hands of the merchant who purchases the musk from the actual hunters, and who then has to transport it, sometimes for a thousand and more miles, to the ports. In his leisurely journey in the caravan the Chinese merchant will skilfully open the pods, insert such adulterants as dried blood, albumen, or earthy matter, and so cunningly close the pods that only an expert can detect that the pod has been interfered with at all. Musk brought into Shanghai was at one time subject to a heavy tax, which was usually paid in kind. If the merchant were so foolish as to offer adulterated pods in payment of the tax, the mandarin did not discuss the matter, but promptly ordered the dishonest merchant to be executed. Hence this "Government" musk was sought after as always being of the very finest quality. Musk is exported from China in small boxes covered with silk and lined with lead. These are known here as cattles or caddies, the name really only signifying the weight of the musk (1 catty = 22 oz.). The amount of musk exported from China varies from about 1,000 to 3,000 cattles per annum.

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matter soluble in alcohol. The moisture ought not to exceed 12 to 15 per cent., and the ash should not exceed 8 per cent. Two ketones of intensely powerful odour have been isolated from musk (*Jour. Prakt. Chem.*, 1906, ii., 73, 488). Of these, muskone, which has the formula  $C_{15}H_{25}O$  (or possibly  $C_{16}H_{30}O$ ), is present to the extent of from 0.5 to 2 per cent. It is a viscid oil of intense musk odour, boiling at  $327^{\circ}$  to  $330^{\circ}$  at 752 mm. It yields an oxime melting at  $46^{\circ}$ , and a semicarbazone melting at  $133^{\circ}$  to  $134^{\circ}$ . The second ketone has not yet been investigated. It is probable that musk entirely owes its odour to these ketones, so it has been suggested that if they are destroyed by oxidation, musk becomes odourless. Bazzoni (*J. Franklin Inst.*, 1915, 463) allowed dry air to pass over a piece of musk weighing 1.32245 mgr. for seven months. With a scarcely appreciable alteration in weight the musk became odourless, and the odour did not return on exposing the musk to moist air. Experiments with such quantities where a claim is made to weigh to  $\frac{1}{1000000}$ th part of a milligram, however, carry little conviction, as it is pretty obvious that the fraction of a milligram of volatile odorous matter had simply evaporated.

Musk is used in perfumery as a fixative, and to impart to perfumes a subtle note which is derivable from no other substance. French perfumers often speak of this as the "*odeur de bête*." At all events, it produces the effect that scarcely anything but animal substances will. The following is the method given by Poucher ("*Perfumes and Cosmetics*," p. 188) for the preparation of the musk for use. A pod of blue pile musk is taken and the grains removed; the outer skin being cut up into small pieces and the whole mixed intimately. This is transferred to a suitable receptacle containing a 5 per cent. solution of glycerine in distilled water. It is macerated, with frequent shaking, for two days, when the clear supernatant liquid is poured off and reserved. The "bottoms" are again twice exhausted with a similar solution, to which has been added traces of alkali. These solutions are then mixed, and about 10 per cent. of alcohol added as an additional preservative, the solution being stored in a perfectly air-tight vessel. The partially exhausted musk is now plunged into otto of rose or clary sage oil, and heated to  $60^{\circ}C$ . for twenty-four hours. The marc is then pressed, and afterwards reduced to a coarse powder, which is macerated in absolute alcohol for a week with frequent shaking. The alcohol solution is filtered into the aqueous extract, and this constitutes a strong tincture, in which

the whole of the odoriferous principles of the musk pod are contained. If it is desired to retain the solution in a semi-weak state, it is advisable either to increase the alcohol to about 60 per cent. strength or to add sufficient glycerine to make a 10 per cent. solution. The addition of the latter will increase the solubility of the extract and also help to preserve it. Durvelle ("The Preparation of Perfumes and Cosmetics," p. 102) gives the following method for preparing the infusion of grain musk. Take 33 grams of powdered musk, and rub into a fine powder, with an equal quantity of sugar of milk in a slightly warmed mortar. Two hundred c.c. of a 1 per cent. solution of potassium carbonate and 300 grams of alcohol are then added, and the mixture rubbed into a cream. Alcohol to 7 litres is then added, the mixture well stirred, and allowed to settle. The particles which have not been sufficiently powdered settle quickly to the bottom; the liquid is decanted and the coarser particles are subjected to a second trituration until they are completely powdered, and the extract is made up to 7 litres if any alcohol has been lost by evaporation. A few drops of ammonia are added, and the mixture is allowed to stand, with periodical shaking, for at least three months. Better results, however, can be obtained if a percolator be used, and the first percolate returned to the percolator four or five times. A product of great delicacy is obtained in this manner. One litre of alcohol is used for 35 to 40 grams of musk, so that the extract is a stronger one than that described above. After the first litre of alcohol has been obtained by five re-percolations, a second quality extract is yielded by repeating the treatment, and after this a third quality, but the last-named is generally used as if it were alcohol, to start operations again on a fresh portion of musk.

There are numerous substances which possess a more or less musky odour, but few of them have any commercial importance. The so-called "American" musk is the product of a gland attached to a caudal appendix in the musk rat, *Fiber zibeticus*. It is obtained by cutting up the gland into small pieces and mixing slaked lime (4 grams per gland) with the tissues. The mixture is macerated in alcohol, and an infusion is thus obtained after a fortnight's treatment. A musk-like substance is said to be produced in Brazil from certain secreting glands of the female iguana. This animal is provided with four such glands, two in the head under the throat, and two—one on each side—in the loins. The "musk" occurs in the form of a very thick paste,

yellowish in colour, and of a distinctive penetrating odour. The natives of Brazil call this substance "lizard musk."

The seeds of *Hibiscus Abelsonius*, known as ambrette seeds, yield an essential oil having a musk-like odour. The seeds are also known as "musk seed." (See "Ambrette, Oil of.")

The dried root of *Ferula sumbul*, known as "musk root," yields from 0.25 to 1 per cent. of a fragrant essential oil having distinct musk odour. The oil has a specific gravity 0.932 to 0.964; optical rotation,  $-6^{\circ} 20'$ ; and ester value, 20 to 90.

In French Guiana the wood of *Guarea grandiflora* is known as musk wood, and also, possibly on account of the similar perfume secreted by the female alligator (see above), as alligator wood. All parts of this tree, especially the bark, smell strongly of musk.

*Mimulus moschatus*, the cultivated musk plant, has a strong musk odour, but is not used to any extent in perfumery.

The following account of the loss of the musk odour in this plant by E. M. Holmes is of great interest (*Chemist and Druggist*, February, 1924, 258):—

"It is now impossible to purchase in any nursery plants of the old-fashioned sweet-scented musk. The absence of odour in the cultivated musk plants has been noticed during the last forty years. The plant is a native of British Columbia, Montana, Oregon, and California. It was sent home to this country by the botanical collector Douglas about 1825, and was described by Dr. J. Lindley in the *Botanical Register* in 1827 (p. 1118). But the curious fact comes out on inquiry that the *scented* musk plant is practically unknown in the countries where it is indigenous, all the plants met with having either no odour, or a scarcely perceptible one, and the fragrant musk plants sold by the florists in these districts have been grown from seed obtained from English nurserymen, and are, so far as is known, all descendants of Douglas specimens. The plant first introduced by Douglas must have been a mutation or sport, from which all other fragrant specimens have been descended. But for fifty years, or up till about 1883, no mention is made by growers of the plant losing its perfume, and in my opinion it is doubtful if it ever has, but rather that it has died out in nurseries and gardens and its place been taken by seed from British Columbia, which was collected from the indigenous scentless forms. The reasons for supposing this are as follows. I have been promised specimens of the *scented* plant by more than one person in whose garden it has remained for the last forty or fifty years up to the present date." Abo

the year 1877 an amateur gardener at Leicester crossed the musk plant with the monkey flower (*Mimulus luteus*), and obtained a hybrid resembling musk, but with larger flowers. This was taken up by Mr. Harrison, a florist at Leicester, and introduced under the name of Harrison's musk. Florists usually take up new, and therefore more expensive and profitable, plants, and consequently do not trouble about the older varieties, which often die out.

I wrote to a friend at Leicester and asked him to inquire if Harrison's musk was scented, and if it could be propagated by seed. A letter from Mr. J. Harrison to my friend, bearing date January 7th, 1924, states: 'I introduced Harrison's musk many years ago, but I have not seen any of it for some years now. I am afraid it is lost. I examined the flowers many times, but could never find a seed pod; therefore I put it down as a 'mule' condition, but never closely examined the internal organs of the flower to see what the real defect was. It has never been noticed to have any musk scent with it, and I cannot give my opinion why the old perennial musk has lost its scent, which is reported in the horticultural papers for some time past.' If Harrison's musk died out or, having no scent, was discarded, it would be only natural that florists should endeavour to get the seed of the musk plant from the country of which it is a native (in ignorance of the fact that *Mimulus moschatus* is only a fragrant form, and was practically unknown in its own country), and such seed supplied to growers would naturally produce scentless musk, and the absence of scent would then attract attention, if my theory is correct. The statements that have appeared in the Press need very careful sifting to afford proof that the actual scentless plants were really the descendants of the fragrant form of the plant."

**MUSK, ARTIFICIAL.**—Although the odour of natural musk to most people somewhat objectionable, as are practically all animal odours, its extreme perfume and fixative values when diluted have for many years past caused attempts to be made to produce the odour by artificial methods. To-day we have so-called artificial musks in plenty, but none of these is either identical with or even similar to the natural odour bearer of true musk. All that can be said of them is that they have a musk-like odour. In every case this odour is so powerful that, unless employed with the greatest restraint as to amount, the resulting perfume will be coarse, vulgar, and objectionable, especially when the more volatile constituents have evaporated. Before the

## PERFUMERY

discovery of the series of bodies which we now term "artificial musks," various unscientific and empirical attempts had met with some success in giving an indefinite mixture which had an odour somewhat resembling musk. According to Kopp (*Geschichte der Chemie*, iv., 395), Margraff in 1759, and Elsner in 1842, took rough amber, powdered it and mixed it with sand, and then distilled it in an iron retort. The oil distilling over was separated, washed, and rectified in the presence of water, and then digested with fuming nitric acid. The complex mixture of nitration products is dried and powdered, and then has a musk odour. (See also *Jour. Prakt. Chem.*, 1842).

Von Gerichten in 1878 observed that the brominated and chlorinated nitrocymenes possessed a musk odour (*Berichte*, xi., 1092). In 1881 Kelbe isolated metabutyl-toluene from the light resin spirit obtained by distilling common rosin, and paved the way for later work by nitrating its homologue isopropyl toluene, which had a marked musk odour. It was not till 1888 that Baur announced the discovery of the first artificial musk of any real value (*Berichte*, xxii., iii., 363). He had taken up the work where Kelbe left it, and succeeded in making *meta*-pseudo-butyl toluene synthetically, and then, nitrating this body, obtained a nitro compound of powerful musk odour. In 1894, Mallman discovered the first ketonic body of musk odour, and since then various other bodies of similar odour have been prepared.

As Gattefossé points out ("Nouveaux Parfums synthétiques," Paris, p. 180), the work of Baur, followed by that of Meyer, Sack, Bischler, Nochting, and Pommier, has practically demonstrated that all the synthetic musk products are based upon the nitration of a body containing a benzene nucleus.

Commercial artificial musk, in the main, is found in three distinct varieties. These are known as (1) musk xylene (or xylol), (2) ketone musk, and (3) musk ambrette.

In addition to these, aldehyde musk, cyano musk, and azido musk will be referred to.

The first of these synthetics to appear on the market was musk xylene, which was patented by Baur in this country in 1889 (No. 4963). The complete specification contained the following instructions:—

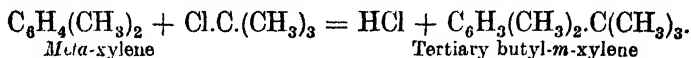
"Toluene is mixed with a haloid combination of butane and boiled, with the addition of chloride or bromide of aluminium. Water is added to the product, and it is then distilled with steam, and that portion which distils over at a temperature between

170° and 200° is taken and treated with fuming nitric acid and fuming sulphuric acid. The resulting product is washed with water and crystallised from alcohol. The product may be dissolved in alcohol, and on addition of a small quantity of ammonia or an ammoniac will exhibit all the essential properties of a tincture of musk. For carrying the invention into practice, 5 parts of toluene are mixed with 1 part of butyl bromide, or butyl chloride or butyl iodide, and to these may be added gradually, whilst boiling,  $\frac{1}{2}$  part of aluminium chloride or aluminium bromide; this results in the development of hydrobromic acid, or hydrochloric acid, or hydriodic acid respectively, and a product of reaction is obtained from which, by the action of steam, the hydrocarbon  $C_{11}H_{16}$  and unchanged toluene are distilled. By the admission of steam the hydrocarbon is carried over, and may be obtained in a condenser as a colourless oil floating on the water. The oil, removed and dried by means of chloride of calcium, is fractionated, and in this manner the necessary hydrocarbon for the production of artificial musk is obtained, 100 parts of the former giving a like quantity of musk preparation. Three parts of fuming nitric acid of 1.52 specific gravity and 6 parts of fuming sulphuric acid are mixed together, and to this mixture is carefully added, whilst cooling, 1 part of the hydrocarbon afore-said. Each drop causes a violent reaction. As soon as all the hydrocarbon is added, the whole mixture is heated up to a temperature of about 100° C. After cooling, the nitro product is precipitated by pouring into cold water of about five to six times the volume, and is separated from superfluous acid by washing with cold water. The nitro product separates first as a viscid, heavy oil, which after some time hardens into a firm crystalline substance. The raw nitro product is then purified by recrystallisation from alcohol of 90 per cent. strength. The purified product crystallises out in yellowish-white needles possessing a strong odour of musk."

III. Xylene musk, the original "musk Baur" of commerce (which, however, was at first sold in a 10 per cent. dilution with alcohol), is the trinitro derivative of tertiary-butyl xylene. It is made from *meta*-xylene as its starting point. This body is condensed by mixing 1,500 grams of isobutyl chloride, 4,500 grams of *meta*-xylene, 30 grams of pure aluminium chloride, and 100 grams of aluminium shavings in an enamelled vessel. The reaction is complete in a few hours, and the mixture is poured on ice water, washed first with water, then with dilute caustic

## P E R F U M E R Y

soda solution, and rectified. The portion boiling between 196° and 210° is reserved for nitration. The reaction is as follows:—



The isobutyl chloride is transformed into the tertiary chloride by a molecular rearrangement. A mixture is then made by gradually adding 1,000 grams of this hydrocarbon to 2,250 grams of fuming nitric acid, and then gradually adding 2,500 grams of fuming sulphuric acid, the mixture being kept at 70° for three hours. The residue, well washed with water, is recrystallised from benzene, and then from alcohol. It melts at 113°. Neither *ortho*- nor *para*-xylene yields similar musk-like bodies.

The formula of musk xylene is therefore  $\text{C}_6(\text{CH}_3)_2(\text{C}_4\text{H}_9)(\text{NO}_2)_3$ . The ketone musk of commerce is rather weaker, but much finer in odour, than musk xylene. Baur showed (*Berichte*, 1898, xxxi., 1344; 1900, xxxiii., 2562; German Patent 87130) that butyl toluene and butyl-xylene react with acid chlorides in the presence of aluminium chloride, giving ketonic derivatives. The recognised ketone musk of commerce is the dinitro derivative of butyl-xylyl-methyl ketone. This body has the formula  $\text{CH}_3.\text{CO}.\text{C}_6(\text{C}_4\text{H}_9)(\text{CH}_3)_2(\text{NO}_2)_2$ . It melts at 136° when quite pure. The corresponding compound prepared from butyl toluene has the formula  $\text{CH}_3.\text{CO}(\text{C}_6\text{H}_5)(\text{C}_4\text{H}_9)(\text{CH}_3)(\text{NO}_2)_2$ , and melts at 131°. It is probable that many commercial ketone musks contain the two bodies. For the preparation of ketone musk, 1,500 grams of butyl-xylene are mixed with 12 grams of carbon disulphide. To this are added 1,300 grams of freshly prepared aluminium chloride, and then 1,000 grams of acetyl chloride, in small portions, the temperature being kept below 45°. When the greater part of the hydrochloric acid has been evolved, the temperature is raised to 60° for a short time, and the reaction mass is then poured on to ice water and washed with water, and then with dilute caustic soda. It is then distilled with steam, and the butyl-xylyl ketone is collected at about 265°. It melts at 48°. This body is then nitrated, the dinitro derivative resulting, which melts at 136°. This ketone musk is sometimes termed musk Mallmann, but apparently incorrectly. Mallmann took out an English patent (4018 of 1894), which appears to have been refused in France and Germany, for a trinitro derivative of isobutyl-tolyl-ketone. Noelting and Clairmont have, however, shown that these nit derivatives had no musk odour.

Musk ambrette is regarded as the finest of all the artifici



musks. Baur found that nitrated butyl-*meta*-cresol or its ethers have a fine musk odour, whereas the corresponding derivatives of *ortho*- and *para*-cresol are odourless. To prepare the typical compound which is known in commerce as "musk ambrette," namely, the tri-nitro-*pseudo*-butyl-*meta*-cresyl methyl ether, 1,100 grams of *meta*-cresol are neutralised with caustic soda solution, and 1,300 grams of dimethyl sulphate are gradually added at a temperature of about 30°. A litre of water is then added and the temperature raised to 75° for an hour. The methyl ether rises to the surface of the liquid, and is extracted with petroleum ether, washed, and rectified. A mixture of 2,400 grams of the methyl ether and 300 grams of aluminium chloride is then introduced into an enamelled vessel, and a mixture of 1,600 grams of isobutyl chloride and 800 grams of the methyl ether is gradually added. Hydrochloric acid gas is evolved, and the mixture becomes crystalline. The mixture is allowed to cool, and is then heated on the water bath for several hours. The reaction mass is then poured on to ice, washed with weak alkali, and distilled. The butyl derivative boils at about 228°. To 1,500 grams of this are added 1,400 grams of nitric acid mixed with 2,000 grams of acetic anhydride, the temperature being kept at 0°. It is then warmed, washed with water, and recrystallised from alcohol. The formula for musk ambrette is  $C_6(NO_2)_3.(CH_3)(O.CH_3).C(CH_3)_3$ . It melts at 85°.

By the oxidation of butyl-xylyl methyl ketone, the basic substance for the preparation of ketone musk, a glyoxylic acid results, from which, by the loss of carbon dioxide, the corresponding aldehyde is obtained. This body has the formula  $C_6H_2(CH_3)_2CHO).C(CH_3)_3$ . It forms a dinitro derivative melting at 112°, of strong musk odour. This body is known as aldehyde musk, but rarely, if ever, met with in commerce (*Berichte*, 1899, xxxii., 447; German Patent 94019 of 1896). Cyano musk and isocyan musk have also been prepared, but are not met with commercially.

It must be borne in mind that artificial musk of commerce is sometimes a mixture of homologous bodies, so that the melting point may not correspond with that of any one of the bodies described. The principal fraud in these substances is the adulteration with acetanilide, which is detected by recrystallisation in hot water, when the crystals separating out will show a different melting point from that of the original sample and will give the well-known phenyl-isocyanide reaction, emitting the

## P E R F U M E R Y

characteristic foul odour when heated with caustic potash solution and a few drops of chloroform. If a specimen of artificial musk shows an indefinite melting point which is lower than that indicated above, and if acetanilide is absent, it is probable that a lower grade of artificial musk is present. For example, musk ambrette is sometimes adulterated with musk xylene. The melting point is considerably lowered and is not at all sharp. Such samples should be recrystallised from warm alcohol, and the melting points of the successive crops taken. The first crystals to separate will melt at a considerably higher melting point—approximating to that of musk xylene—and the true musk ambrette will crystallise later, other impurities crystallising last.

For further details of the various rarer forms of artificial musk, see W. A. Noeltling (*Chemie et Industrie*, 1921, 6, 719), and also the following references, which are there included:—

### *German Patents*

- 47599/1888. Nitration of butyl toluene.
- 62362/1891. Cresol musk.
- 72998/1893. Nitration of aryl-methanes with elimination of  $\text{CH}_2$ .
- 67299/1893. Butylation and nitration of dihydroxylene.
- 80158/1894. Hydrindene musk.
- 84336/1894. Cyano musk.
- 86447/1895. Butylation and nitration of *meta* haloid toluenes.
- 87130/1894. Ketone musk.
- 90291/1895. Nitration of haloid butyl-xylenes.
- 94019/1896. Aldehyde musk.
- 99256/1897. Azido musk.
- 69072/1890. Butyl-xylyl sulphonic acid.
- 184230/1906. Butyl-xylene from isobutylene.

Full references to the original literature of the subject will be found in the paper by Noeltling above quoted.

The best solvents for the artificial musks are the esters benzy benzoate and ethyl phthalate.

For the detection of small quantities of artificial musk in perfumes, see "Nitro Compounds, Detection of."

**MUSKONE.**—See "Musk."

**MYRCIA OIL.**—See "Bay Oil."

**MYRISTICA.**—See “Nutmegs.”

• **MYRISTICIN.**—This body is an allyl-methoxy-methylene-dioxybenzene, of the formula  $C_{11}H_{12}O_3$ . It is present in nutmeg, mace, and parsley oils. It is a fragrant liquid, with a nutmeg odour, boiling at  $150^\circ$  at 15 mm., and having a specific gravity 1.45, and refractive index 1.5403. It yields a dibromide melting at  $109^\circ$ , and on oxidation yields myristic aldehyde, melting at  $130^\circ$ , and myristic acid, melting at  $210^\circ$ .

**MYRRH.**—The genuine myrrh of commerce is that known as herabol myrrh. The so-called bisabol myrrh is a different substance altogether (see “Frankincense”). Myrrh is a gum resin obtained from the stem of *Balsamodendron myrrha* and other species, and also probably from species of *Commiphora*. The stem wounded and a yellowish liquid exudes, which soon solidifies to reddish-brown or blackish masses. It is collected in Arabia, Abyssinia, and Somaliland, and arrives on the London market in chests containing very mixed qualities, which are known as “sorts.” These are then often separated into several grades. It occurs in small masses of a yellow to yellowish-red colour, black pieces being of inferior quality. The masses vary in size from that of a pea to that of a chestnut. An alcoholic solution of myrrh is used to a considerable extent in the manufacture of dental washes, and it is also used as a constituent of heavy floral odours such as broom and honeysuckle, and as a fixative in odours of the so-called Oriental type. It is also used in incense and in Chinese joss sticks.

Myrrh has been examined by von Friedrichs (*Arch. Pharm.*, 1909, 245, 427), who states that it contains three resin acids soluble in ether,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -commiphoric acids. The first two are isomeric, of the formula  $C_{14}H_{18}O_4$ , whilst  $\gamma$ -commiphoric acid is the formula  $C_{17}H_{22}O_5$ . A resin ester of commiphoric acid,  $C_{28}H_{38}O_8$ , is also present. Two phenolic resins were also isolated, herabomyrrhol,  $C_{18}H_{26}O_5$ , and  $\beta$ -herabomyrrhol,  $C_{20}H_{26}O_6$ . A volatile alcohol,  $C_{14}H_{22}O_2$ , and a resene, heraboresene  $C_{42}H_{56}O_8$ , present in small quantity. Two resin acids insoluble in ether were separated,  $\alpha$ -myrrholic acid,  $C_{15}H_{22}O_7$ , and  $\beta$ -myrrholic acid,  $C_{15}H_{20}O_7$ .

In addition to these resin constituents, which amount to from 20 to 40 per cent., there is present from 50 to 60 per cent. of a extrorotatory gum, from 2 to 8 per cent. of essential oil, and about 4 per cent. of ash. (The formulæ above given must be

## P E R F U M E R Y

Both the bark and the leaves of the nutmeg tree yield small quantities of essential oil, but neither contains any particularly fragrant constituents.

**OAK MOSS RESIN.**—See “Mousse de Chêne.”

**OCOTEA OILS.**—The essential oil of *Ocotea caudata* is a highly odorous oil. (See “Bois de Rose Oil.”) *Ocotea usambarensis* is a tree known as the Ibean camphor tree, and the essential oil distilled at Amani (German East Africa—as it was before the Great War), has been examined by Schmidt and Weilingner (*Berichte*, 1906, **39**, 652). The bark of this lauraceous tree yielded 0·15 per cent. of oil having the following characters:—

|   |               |
|---|---------------|
| Specific gravity at 20° . . . . .                           | 0·913         |
| Boiling range at 10 mm. . . . .                             | 50°-160°      |
| Optical rotation . . . . .                                  | — 11° 12'     |
| Refractive index . . . . .                                  | 1·4760        |
| Acid value . . . . .  | 1·2           |
| Ester value . . . . .                                       | 12·5          |
| Free alcohols (C <sub>10</sub> H <sub>18</sub> O) . . . . . | 4·5 per cent. |

The oil contains myristic aldehyde, cineol, terpineol, and a sesquiterpene. Three oils distilled from the wood were examined at the Imperial Institute (*Bull. Imp. Inst.*, 1911, **9**, 340) and found to have the following characters:—

|                                | 1        | 2        | 3        |
|--------------------------------|----------|----------|----------|
| Specific gravity . . . . .     | 0·964    | 0·968    | 0·933    |
| Optical rotation . . . . .     | — 7° 30' | — 7° 30' | — 0° 28' |
| Saponification value . . . . . | 30·1     | 30·1     | 13·3     |

The so-called Venezuela camphor wood oil is probably distilled from the wood of a species of *Ocotea*. It has a specific gravity 1·155, and optical rotation + 2° 40'. The oil has an odour resembling that of the oil of *Isarum canadense*, and sets at ordinary temperatures to a crystalline mass. The crystals, which form about 90 per cent. of the oil are apiol, probably identical with the apiol extracted from parsley oil.

**OCTINE CARBONATES.**—See “Heptine Carbonates.”

**OCTYL ACETATE.**—This fragrant ester has the formula CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>O·OC·CH<sub>3</sub>. It is an oil boiling at 209°, of specific gravity 0·885. It occurs naturally in the oil distilled from wild parsnip seeds, and may be prepared by the acetylation of normal octyl alcohol (*q.v.*). It has a fruity-floral odour, recalling orange and jasmine, and is useful for preparing artificial flower oils, but must be used in traces only.

**OCTYL ALCOHOL.**—Normal octyl alcohol,  $\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{OH}$ , exists in the essential oils of heracleum, and in other oils, in the form of esters. It is a liquid of specific gravity 0.828, and boils at  $196^\circ$  to  $197^\circ$ , or at  $96^\circ$  at 17 mm. It has a pleasant odour, recalling that of opoponax. It is prepared by saponifying coconut oil and extracting the free fatty acids. These are esterified by means of methyl alcohol, and the esters are fractionated. At about  $85^\circ$ , at a pressure of 25 mm., the main constituent distilling over is methyl caprylate. By reduction with sodium and alcohol, normal octyl alcohol results. A secondary octyl alcohol,  $\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{OH})\text{CH}_3$ , results from the distillation of methyl ricinate. The oxidation of primary or normal octyl alcohol gives octyl aldehyde, whereas secondary octyl alcohol yields the ketone octanone-2, a substance sometimes improperly described as octyl aldehyde (*q.v.*).

**OCTYL ALDEHYDE.**—The eight-carbon normal aldehyde  $\text{CH}_3(\text{CH}_2)_6\text{CHO}$  is prepared by the regulated oxidation of normal octyl alcohol, the secondary alcohol yielding a ketone, octanone, which is quite different from octyl aldehyde. The aldehyde occurs naturally in neroli and rose oils, and has a deep honey-like odour. It is useful in the blending of floral perfumes. Its specific gravity is 0.826, or when absolutely pure 0.821; refractive index, 1.41955, and boiling point,  $82^\circ$  at 13 mm. At low temperatures it solidifies, melting at  $13^\circ$  to  $16^\circ$ . It yields an oxime melting at  $60^\circ$ , a semicarbazone melting at  $101^\circ$ , and a naphtho-cinchoninic acid compound melting at  $234^\circ$ .

**OCTYL BUTYRATE.**—This ester,  $\text{CH}_3(\text{CH}_2)_7\text{OOC}(\text{CH}_2)_2\text{CH}_3$ , is present in a few essential oils, such as male fern oil, and has a powerful fruity odour. It boils at  $244^\circ$ .

**OCTYL FORMATE.**—This ester, which resembles the acetate in odour, has a specific gravity 0.882; and boils at about  $198^\circ$ .

**OCTYL HEPTYLATE.**—This is the highest ester of octyl alcohol which can be employed usefully as a perfume. Its formula is  $\text{CH}_3(\text{CH}_2)_7\text{OOC}(\text{CH}_2)_5\text{CH}_3$ . Its odour is powerful and fruity, but somewhat heavy.

**OCTYL VALERIANATE.**—This ester, which has a very fruity odour, is a mixture of isomers (of esters of valerianic and isovalerianic acids). The commercial article has a specific gravity 0.869, and boils at about  $266^\circ$ .

**ODOUR AND CHEMICAL CONSTITUTION.**—The

## PERFUMERY

factors which govern the odour of a body are apparently three in number; the incidence and nature of two of these three factors are more or less universally accepted, but the third is still the subject of much speculation and controversy.

In order that a substance shall evince an odour, it is first necessary that it shall be sufficiently volatile to ensure its transmission to the olfactory region of the nose; a substance that is nonvolatile *ipso facto* is odourless. Further, it is necessary that the substance shall be sufficiently soluble in the aqueous and fatty layers that protect the nerves of the nose, as otherwise these layers form barriers which the substance cannot penetrate. Thirdly, some sort of action must take place between the substance and the nerves when they come into contact.

Two theories have been advanced regarding this action, one of which relates the phenomenon to chemical reaction between the odoriferous substance and the materials which occur in or near the nerves, while the other supposes "valency electronic" vibrations to cause resonant vibration of the nerves.

The chemical theory is known as the "residual affinity theory of odour," and is based on the fact that every odoriferous body possesses in its molecule some atom whose valencies are not fully satisfied. This seems to be the keynote of the whole subject, and is set forth fully in E. J. Parry's "The Chemistry of Essential Oils and Artificial Perfumes," vol. ii., 4th ed., chap. ii., and also in *The American Perfumer*, 1923, pp. 345, 405. This chemical theory visualises actual chemical reaction between the odoriferous substance and the "osmoceptors" in the nose.

The electronic theory ascribes the phenomenon to the electrical state of the molecule resulting from the revolving electrons of the atom: the revolution of these electrons is supposed to cause resonant vibrations which induce sympathetic vibrations in the nose nerves.

In this connection, it is interesting to note that Tashiro has recently proved that nervous impulse is a chemical reaction, and not primarily a physical one.

The main facts which need to be considered are briefly set out below. Only those substances which possess elements having variable valencies can evince odours, such elements being sulphur, selenium, phosphorus, arsenic, antimony, halogen, carbon, nitrogen, oxygen; and the greater this variability, the greater the "osmophoric" power; thus carbon, the valency of which seldom varies, is only a feeble osmophore, while sulphur is a powerful one.

These elements are all closely associated in the periodic table of elements, and are apparently only osmophoric when not employing their full valency. The majority of elements, although possessing variable valency, are nonosmophoric because their compounds do not possess the essential concomitant physical characteristics of volatility or solubility. These defects are not necessarily inherent in the atom itself, but may be due to its manner of combination; thus arsenic, when functioning as a metal, does not yield odoriferous compounds, but when part of a radicle, frequently gives rise to bodies of great pungency.

If in an odoriferous body the atoms with which the possibility of unsaturated or residual affinity exists could be replaced by others where such affinity does not exist, the odour would be removed: thus cacodyl and ethyl hydrogen selenide would each yield the odourless ethane, methyl iodide would give methane, and acroleine the almost odourless propylene, and so on.

As regards the actual phenomena of the process of smelling, the following facts have to be accounted for: (1) An odour can only be perceived during inhalation, and it only persists for a brief interval after the inhalation has been completed. This appears to show that the substance undergoes some rapid change, and that its odour is not merely due to its presence. (2) The nose rapidly becomes insensitive and unable to perceive the odour of a substance without a rest. This indicates that some change has taken place in the nose itself. (3) The same substance may have a different odour when smelt in a concentrated form from that which it has when smelt in a dilute form, indicating that the action is not a simple one.

A complete bibliography of the subject has recently been published under the title of "Osmics." T. H. D.

**ÆNANTHYLIC ALDEHYDE.**—This body is also known as ænanthol, or heptylic aldehyde (*q.v.*).

**ÆNANTHYLIC ETHER.**—See "Ethyl Heptoate."

**OLEANDER LEAF OIL.**—The leaves of *Nerium oleander*, belonging to the natural order *Apocynaceæ*, yield 0.025 per cent. of an essential oil having a strong spicy odour. Its constituents have not been identified.

**OLEA FRAGRANS.**—The flowers of *Olea fragrans*, which are known in China as *Kwei Hua* (*Kouei Rhou*), are used for perfuming tea. This flower is probably the most popular perfume flower in China, and is largely cultivated throughout the country.

The flowers are in clusters about as large as a spray of lilac, and their fragrance somewhat resembles that of jasmine. There are two varieties, the flower being yellow in one case and brown in the other. Although the essential oil has not been extracted and examined, some idea of the richness of the perfume may be gathered from the fact that a single tree when in bloom is capable of loading the air of a fair-sized garden with an intense, delicious perfume.

**OLEIC ALDEHYDE.**—This aldehyde,  $C_{17}H_{33}CHO$ , is present in oil of orris root. It boils at  $168^{\circ}$  to  $169^{\circ}$  at 4 mm., and has a specific gravity 0.8513, and refractive index 1.4557. It forms a semicarbazone melting at  $87^{\circ}$  to  $89^{\circ}$ .

**OLIBANOL.**—According to Hänsel (*Chem. Zentral*, 1908, i., 1837, ii., 1437), oil of olibanum (see "Boswellia Resins") contains an alcohol of the formula  $C_{26}H_{44}O$ , which he named olibanol. It is a viscid oil which possesses a strong odour of olibanum. It boils at  $334^{\circ}$ , has a specific gravity 0.9570 to 0.9596 at  $20^{\circ}$ , and optical rotation  $-65^{\circ}$  to  $-71.5^{\circ}$ . Fromm and Autin, however (*Annalen*, 1913, 401, 253), apply the name olibanol to a substance of specific gravity 0.9525 and boiling at  $211^{\circ}$ , of the formula  $C_{16}H_{16}O$ , which appears to be a keto-alcohol. (See also Fromm and Klein, *Annalen*, 1921, 425, 208.)

**OLIBANUM.**—See "Boswellia Resin."

**ONDRATA ZIBETHICA.**—This amphibious animal is the Canadian musk-rat, and is related to the beaver. It abounds, according to Sawyer ("Odorographia," i., 11), on the margins of lakes and rivers of the United States and Canada, inhabiting mud huts which it builds for itself. It lives on aquatic plants. Its peculiar musk odour is due to a whitish fluid secreted in certain glands near the base of the tail. A small amount of the skin and tail, etc., of this animal may be used locally for perfumery purposes, but although it yields a tincture of powerful musk odour, the secretion does not find its way into commerce.

**OPOPONAX.**—There has been much confusion in regard to this gum-resin, which, however, has been cleared up by E. M. Holmes. There is a gum-resin known as opoponax which has been to some small extent employed in medicine. This is the true opoponax, which has a penetrating, disagreeable odour recalling that of crushed ivy leaves. It has nothing in common with the "opoponax" of perfumery, the botanical origin of which has long been doubtful. The essential oil, which is obtained to



## P E R F U M E R Y

the extent of about 8 per cent. from the gum-resin, has been examined by Tucholka (*Arch. Pharm.*, 235, 289). It is a fragrant oil, of specific gravity 0.870 to 0.905; optical rotation about  $-14^{\circ}$ ; and refractive index, 1.4890 to 1.4940. The only constituents so far identified are a sesquiterpene, which has been termed bisabolene, and a sesquiterpene alcohol which boils at  $135^{\circ}$  to  $137^{\circ}$  at 2 mm. pressure. The gum-resin itself has the following characters:—

|                                      | Per cent. |
|--------------------------------------|-----------|
| Gum soluble in water . . . . .       | 22.1      |
| Gum soluble in alkali . . . . .      | 29.85     |
| Resin . . . . .                      | 21.5      |
| Essential oil . . . . .              | 7.8       |
| Water . . . . .                      | 3.17      |
| Insoluble vegetable débris . . . . . | 13.4      |

The following details as to its actual botanical origin are given by E. M. Holmes (*P. & E. O. R.*, 1924, 4). He prefers to call the opoponax of perfumery “sweet myrrh” or “bisabol,” and proceeds as follows:—

“One of the most interesting facts about sweet myrrh is that, although it has been an article of Eastern commerce since the time of Moses, if not earlier, and has been used in China from time immemorial up to the present, for China is still the largest buyer of it, yet it is so little known in Europe that, on the rare occasions when it appears in the London market, it has been offered as opoponax, or as a ‘sort of bdellium.’ As recently as 1879 Flückiger says of bisabol: ‘This drug is of African origin, but of the plant that yields it nothing is known.’ However, the following note occurs in the *Kew Gardens Report* for 1879, p. 40: ‘A complete set of plants yielding the several kinds of myrrh known in Eastern commerce were received at Kew from Mr. Wykeham Perry, who obtained them from Captain Hunter at Aden. Of *bisabol* Mr. Wykeham Perry has sent two specimens, and these, fortunately, have produced abundance of foliage. They cannot be botanically identified with any certainty at present, and, indeed, the species may be hitherto undescribed. It, however, is closely allied to *Balsamodendron Katuf* Kunth. He had only seen it in Arabia in a cultivated state. By the Somali the tree is called *hadi*, and the gum *habbak-hadi*; it is purchased by Indian merchants for export to Bombay, and is by them called *bisabol*. It is also called *mhaisa bol*, i.e., buffalo myrrh, because it is sometimes given to improve the flow of milk in cows. It is

found only in the centre of the Somali promontory, and not in Arabia at all.' •

"On reading this statement, I went to Kew to see the myrrh plants, and on the stem of one of the two bisabol plants I noticed an exuded drop of the gum-resin, and was courteously allowed by the Director to taste it. I found that it possessed the unmistakable flavour of that drug, and there could be no possible doubt that this plant is the source of it. The leaves I have given an illustration of in the *Pharmaceutical Journal* (4, vol. viii., p. 80, fig. 17). The leaves are nearly free from hairs, like those of *Commiphora Kataf*, but at Kew they are regarded as more probably belonging to the variety *glabrescens* of *C. erythraea* of Engler. The stone of the fruit differs in the two species, but that of the variety *glabrescens* has not yet been described, so that it is not yet certain whether it should be referred to *C. Kataf* or *C. erythraea*, but is provisionally placed under the latter.

"In 1912 some information concerning bisabol was published in a most interesting book on British Somaliland by Dr. R. E. Drake-Brockman, in which he states that the bisabol tree is found only in the Haud, Nogal Valley, and Ogadain districts, that the tree is called *hadi* and the gum-resin *habbak-hadi* by the Somalis, and is brought by the Ogadain caravans to the coast during the winter months *packed in separate skins, and never mixed with the true myrrh*. No Somali, unless he wishes to cheat the trader, ever mixes the cheaper *habbak-hadi* with the true myrrh. The tree grows to a great height, and is one of the largest of the desert trees, but is found only in the western districts of Somaliland. The bark is also collected by the Somali women and used for burning inside their huts, owing to its pleasant smell and supposed medicinal properties. The fruit is sometimes collected and given to camels, as they are said to be very fond of it.

"The bisabol or *habbak-hadi* is brought to the great fair held at Berbera from November to February, and Indian buyers and others from Zanzibar, Aden, Makulla, and Bombay come there to buy myrrh and take some of the bisabol, but the largest proportion of the latter reaches China, where it is employed in the preparation of the joss sticks used like incense in the Chinese temples. But how it reaches China, whether direct from Berbera or indirect *viâ* Zanzibar or Makulla, on the south Arabian coast, is not certain, although Makulla is known to have been a port of call for Chinese ships when the Israelites were captives in Egypt.

## PERFUMERY

At Aden and Bombay, myrrh and frankincense are graded, and some of the bisabol goes there also ; but as it is cheaper than true myrrh, it may be used by merchants for diluting medicinal myrrh. At all events, pieces of bisabol are found in myrrh imported from Aden and Bombay, as well as different varieties of bdellium.

" One of the most interesting facts in connection with bisabol is that it is evidently the myrrh of Scripture, for medicinal or bitter myrrh has never been used as a perfume, and has not a sweet odour when burnt. In ancient times, perfumes, as the word implies (*pēr funum*), i.e., by smoke, were used like incense, e.g., Proverbs, 7, xvii., 'I have perfumed my bed with myrrh, aloes, and cinnamon'; and Canticles, 1, iii., 'perfumed with myrrh and frankincense.'

" It is easy to understand that bisabol might be mistaken at a casual glance for myrrh, as they present much the same appearance, but it could only be mistaken for opoponax by one who has never seen the latter. Bisabol has the same reddish-brown colour and whitish streaks as myrrh, but the taste is much less bitter, and the flavour is absolutely different and quite characteristic. Opoponax has a distinctly unpleasant odour and taste, recalling that of bruised ivy leaves, and has not the whitish streaks and small patches that myrrh has. Perfumed myrrh could easily be obtained pure in its original packages at Berbera, in the Gulf of Aden, during the months of November to February, if asked for under the name of *habbak hadi*, the Somali name, or *bisa-bol*, the name used by the Indian traders who buy it, and who distinguish the medicinal myrrh by the name of *heera-bol*."

**ORANGE-FLOWER WATER.**— See also under "Neroli Oil."— Orange-flower water is the aqueous distillate separated from the essential oil of neroli in the manufacture of that oil. Its odour approximates more nearly to that of the natural flowers, for the reason that is given below. The water is of great use in the manufacture of perfumes of the eau de Cologne type, as the use of such a perfumed water instead of ordinary water for the dilution of alcohol results in a considerably superior preparation. It is practically colourless, but darkens with keeping. In order to keep it in its best state of preservation, it should be stored in a cool, dark place, in containers full, with the air carefully excluded.

In orange-flower water, all the constituents of neroli oil (*q.v.*) are present, many only in traces. But the proportions present are obviously entirely altered on account of the varying solubilities of the constituents in water. Terpenes, for example, are

present in minute traces only, whilst methyl anthranilate, being very soluble, is present in a greatly increased proportion. Phenyl-acetonitrile is also probably present in the water. Since the proportions of the various constituents present in the water are always practically constant, the water being a more or less saturated solution of such constituents, orange-flower water is of much more constant characters than oil of neroli, and certainly represents the odour of the flower more accurately than does the essential oil.

M. Bonis, joint director of the Central Laboratory of the French Ministry of Agriculture, has recently published ("Annales des Falsifications et des Fraudes," through *P. & E. O. R.*, 1924, 290) an elaborate account of this perfumed water and its adulteration. He states that for some years there have been found in commerce so-called orange-flower waters which have consisted, in whole or in part, of a distillate ("eau de brouts") of inferior quality obtained from orange buds, and substitutes have even been offered prepared from artificial neroli oil. Distillers of the genuine article have justly complained of the injury to their industry brought about by these adulterated or factitious waters, and the Service for the Suppression of Frauds has instituted an investigation as to the best means of preventing these fraudulent practices. In order to put the matter in proper perspective, M. Bonis first considers the actual products and their various designations in commerce.

Orange-flower water is a product (with neroli oil) of the distillation of orange flowers, which generally takes place in May. It is saturated with the soluble principles of neroli; and is also called "eau bigarade-pétales" (bigarade-petal water). Two qualities are differentiated:

(1) "L'eau 2 kilos." One litre corresponds to 2 kilos of orange-flower petals. The still is charged with 1,000 kilos of flowers, and enough water is added to allow the recovery of 1,000 to 1,500 litres. The first 500 litres which comes over is the most esteemed and concentrated, and constitutes "l'eau 2 kilos."

(2) "L'eau 1 kilo." The procedure of production is the same, save that 1,000 litres is collected from 1,000 kilos of flowers.

Less concentrated waters than the above are necessarily of less value. Neroli oil is, of course, collected during the process and in the further distillation after these special waters have been separated.

"L'eau de brouts" is made in June, and is a by-product in

making petitgrain oil, which is obtained by distilling the young buds, leaves and ends of the shoots of the orange tree. It is only prepared in one quality, and its value is about half that of orange-flower water.

In commerce the "eau 2 kilos" is called "eau concentrée 2 kilos" and the "eau 1 kilo" K.P.K. (kilo pour kilo), or "eau quadruple." K.P.K. diluted with an equal quantity of distilled water is known as "eau double," or "eau codex." The "eau double," diluted in its turn with a like amount of distilled water becomes "eau simple," which is eight times less concentrated than the "eau bigarade petales 2 kilos." Waters styled "eau triple" or "triple supérieure" are intermediate between the varieties "eau double" and "eau quadruple." There are thus five or six grades of orange-flower water in commerce which differ by their degree of concentration, without, however, their respective ester content being defined.

Leaving aside the question of the source of the water used in distillation (distilled, river or rain), which is easily recognised, and also the question of metallic contamination from prolonged contact with receptacles composed of unsuitable materials such as lead and zinc, it is found that orange-flower oil contains all the constituents of petitgrain oil, with the addition of methyl anthranilate. Further, Professor Giovanni Romeo has recently noted two hitherto unknown bodies in neroli oil, viz., decylic aldehyde and jasmone. The following are common to both oils: Limonene, linalol, linalyl acetate, geraniol, and geranyl acetate. The proportion of these constituents, however, is different; thus neroli contains from 7 to 13 per cent. of esters stated as linalyl acetate, while petitgrain oil contains from 20 to 55 per cent. But on examining authentic samples of the waters, M. Bonis has found that orange-flower water shows appreciable quantities of esters (K.P.K. 0.3 per mille as linalyl acetate), but "eau de brouts" contains no sensible amount. One must therefore assume that the esters of petitgrain are almost insoluble in water, while those of neroli are soluble, or else that the ester index of orange-flower water is almost entirely due to one constituent—methyl anthranilate. In fact, the author has found this ester in notable quantity in orange-flower water, and concludes that the ester index is due entirely to it. Although little soluble in water, methyl anthranilate readily forms soluble salts. Or, in the course of distillation, saponification may take place, giving rise to traces of organic acids, which in their turn produce acetates and

formates. Methyl anthranilate presents the marked characteristic of a violet fluorescence especially visible in an alcoholic solution, and very intense in direct sunlight. In order to show this fluorescence, it is only necessary to add to alcohol (90 to 95 per cent.) a half, or even a quarter, of its volume of orange-flower water.

The above characters are distinct enough to differentiate analytically between orange flower water and "eau de brouts," but they are evidently insufficient to distinguish in cases of mixtures of the two waters. The reaction of Gobley alone appears to present means of identifying natural orange-flower water. This consists of adding to the suspected water a proportion of a mixture of sulphuric and nitric acids, when one obtains a feeble, fugitive rose coloration; it is scarcely visible in a very diluted water, or in one which is very old. Viron's reagent (sulpho-carbazol 0.15 gram, sulphuric acid 100 grams) gives a bright rose precipitate with orange-flower water; but as it gives a somewhat darker one with "eau de brouts," it cannot be considered as specific. The reaction of Lepage depends on the fixation of iodine, "eau de brouts" fixing about twice as much as orange-flower water.

Experiments in the Central Laboratory have proved that Legal's reaction, and Legal's reaction as modified by Duparc and Monnier, give a double test, when taken together, which forms an absolute means of distinguishing natural orange-flower water. Following the Legal test, one successively adds to orange-flower water nitroprusside of sodium, soda solution, and acetic acid. After the addition of the soda a yellow colour develops which changes to light brown in about one minute, after adding the acetic acid an emerald-green colour is evident; the same changes take place with oil of neroli and with methyl anthranilate. If now the modified test of Legal, Duparc and Monnier is used by adding sulphate of zinc to the solution, there forms at the end of the reaction a reddish-violet lake, rising generally to the surface of the liquid; with neroli oil or methyl anthranilate this lake is green or dull yellow. "Eau de brouts" in either case gives no reaction or only a dirty yellow precipitate.

Apparently the two constituents alluded to above—decyllic aldehyde and jasmone—play a part in the reactions.

Technical details of the reagents, and the methods of carrying out the tests are given below.

Reagents :—

(1) Freshly prepared solution of sodium nitroprusside, 10 per cent.

## PERFUMERY

- (2) Solution of caustic soda free from carbonate, 5 per cent.
- (3) Crystallisable acetic acid.
- (4) Solution of zinc sulphate, 10 per cent.

To 10 c.c. of the water to be tested, in an ordinary test tube, add successively (a) 0.5 c.c. solution of sodium nitroprusside, mix, (b) 2.5 c.c. caustic soda solution, mix, and after about fifteen seconds in contact add as quickly as possible (c) 0.5 c.c. acetic acid, rotate the tube rapidly, and add immediately (d) 2 c.c. zinc sulphate solution.

The green colour produced on the addition of acetic acid is very fugitive, and it is necessary to add the zinc sulphate solution before it loses its intensity, as it is only in these circumstances that the formation of the characteristic violet-red lake is clearly observed. The green lake formed in the case of most synthetic waters only appears slowly, some minutes often elapsing before the coloration is seen. Here we have reactions distinguishing between natural orange-flower water and (a) artificial waters or (b) "eau de brouts." It does not seem, in M. Bonis' opinion, essential to have a specific reaction for "eau de brouts" in order to undertake the suppression of fraud, if one has at hand the means, at least approximately accurate, of determining the amount of genuine water present in a mixture, be the diluent distilled water or water from the leaves or from the buds.

With regard to the identification of and estimation of "eau de brouts" in orange-flower water, the question arises of distinguishing between the various grades of flower waters, and it is suggested that possibly a determination of the ester value might yield a solution, as it is almost equivalent to an estimation of the methyl anthranilate contained. To this end a number of experiments have been performed at the Central Laboratory. A very promising method consists of transforming the methyl ester into a red colouring matter by diazotation and copulation with  $\beta$ -naphthol. The brick-red or brownish-red anthranilic acid obtained is insoluble under the conditions of the experiment, and it was hoped that it might be possible to estimate the natural ester by calculation from the weight of the acid, but, so far, impurities in the precipitate have prevented accurate results. The question is being thoroughly examined, both as to the various grades of flower water and the admixture of the petitgrain product.

In conclusion, M. Bonis suggests that if manufacturers must produce so many grades of orange-flower water, they might at

## P E R F U M E R Y

p. 86), the following orchids produce flowers with the typical odour given :—

|                                |  |
|--------------------------------|--|
| <i>Acropera loddigesii</i>     | Scent of wallflowers.  |
| <i>Angræcium fatuosum</i>      | Scent of tuberoses.  |
| <i>Bifrenaria inodora</i>      | Scent of lily of the valley.   |
| <i>Catasetum scurra</i>        | Scent of lemons  |
| <i>Cattleya Eldorado</i>       | Scent of roses (in the evening only).  |
| <i>Cleistoma ionasmum</i>      | Scent of violets.  |
| <i>Cæliopsis hyacinthisma.</i> | Scent of hyacinths.  |
| <i>Dendrobium glumaceum</i>    | Scent of lilac (morning); scent of heliotrope (evening).                     |
| <i>Dendrobium nobile</i>       | Scent of hay (evening); scent of honey (noon); scent of primroses (morning). |
| <i>Epidendrum vulnerum</i>     | Scent of carnations (morning).   |
| <i>Maxillaria aromatica</i>    | Scent of cinnamon.   |
| <i>Odontoglossum citrosum</i>  | Scent of roses.  |
| <i>Odontoglossum gloriosum</i> | Scent of the hawthorn hedge.   |
| <i>Orchis sambucina</i>        | Scent of elder flowers.  |
| <i>Zygopetalum mackayi.</i>    | Scent of hyacinth (during sunshine).   |

Natural orchid perfumes do not exist in commerce, but are mixtures of artificial compounds rounded off with natural flower extracts. As will be seen from the above list, the perfumer has plenty of scope to be original and still keep his composition "true to name." Amyl salicylate, the ester known as *orchidée* or *trêfle*, is the artificial substance upon which orchid perfumes are based. Some perfumers prefer a blend of amyl salicylate with isobutyl salicylate. *Mousse de chêne* is decidedly the best fixative for orchid perfumes.

**ORIGANUM OILS.**—See "Marjoram Oil."

**ORIXA JAPONICA, OIL OF.**—According to Shinosaki (*Jour. Soc. Chem. Ind.*, 1921, 40, A., 560), the leaves and twigs of *Orixa Japonica* yield about 0.01 per cent. of an essential oil resembling kuromoji oil in odour. It has the following characters :—

|                               |        |
|-------------------------------|--------|
| Specific gravity              | 0.8974 |
| Specific rotation             | — 4.5° |
| Refractive index              | 1.4750 |
| Ester value                   | 37.3   |
| Ester value after acetylation | 100.3  |

It contains camphene, linalol, a terpene alcohol, and esters of the two last named.

**ORRIS ROOT.**—The so-called orris root is in reality a



rhizome, but as it is so generally termed "root," that designation may be maintained here. This substance is of extreme value in perfumery, being used to a considerable extent in the form of powder (indeed, the old-fashioned violet powder is a mixture of orris root and starch, with or without a little extra perfume), and in the form of a tincture, an absolute, and a distilled oil.

There are three species of orris (natural order *Irideæ*) which are usually employed for the production of commercial orris root. These are *Iris germanica*, *I. pallida*, and *I. florentina*.

*Iris germanica* is common in the environs of Florence and Lucca, and is also found in central and southern Europe, in northern India, and in Morocco. This is the species most usually cultivated in gardens in the temperate countries of Europe. It has dark blue flowers.

*Iris pallida*.—This plant resembles *Iris germanica*, but its flowers are of a paler colour. It is found wild in the calcareous soils of Istria, and is also abundant in the environs of Florence and Lucca.

*Iris florentina*.—This species bears large white flowers. It is a native of the coast of Macedonia and the south-west coasts of the Black Sea. It is also indigenous to the area surrounding the Gulf of Ismid, and the vicinity of Adalia in Asia Minor. It is also found in the neighbourhood of Lucca and Florence, though it is not indigenous, but merely acclimatised to these last named situations.

The finest roots are produced in Tuscany, and are known commercially as Florentine orris, but it should be remembered that this term does not mean the root of *Iris florentina*, as all three species are used for its production.

The rhizomes are dug up towards the end of the summer, the small roots and growing portions of the plant removed, and the clean rhizomes peeled and slowly dried. When fresh, the rhizomes are nearly odourless, and some change takes place during the slow drying and storing of the rhizomes, which results in the development of the odour characteristic of the orris "root."

The most esteemed variety occurring in commerce is the Florentine rhizome, which is usually prepared with great care, carefully peeled, and is pale in colour and very fragrant.

The Verona root is less esteemed, as it is yellowish in colour, less carefully peeled, and is less bulky. The dried and peeled rhizomes vary in length from 1 to 4 inches, and are white or yellowish in colour, somewhat flattened, and exhibit enlargements

and contractions, each enlargement representing one year's growth. One or two short branches are generally attached to the larger extremity. The under surface bears numerous nearly circular root scars, easily discernible, and the upper surface bears less conspicuous leaf scars or traces of the fibrovascular bundles of the leaves where they have passed from leaf to rhizome. The tissue of the rhizome is firm and compact. On a transverse section the rhizome shows a somewhat narrow cortex, separated by a brownish cambium line from the large stele. The last named contains visible crystals of calcium oxalate.

In powder, orris may be recognised by the starch grains, which are mostly simple, oval or elliptical in shape, and with a distinct branching hilum.

Mogador orris is much darker than the Italian rhizome, and is much less valued than the latter. Indian orris is poor in quality, having but little aroma.

Originally the roots were derived from wild plants, but to-day considerable plantations of cultivated orris exist.

The three species of iris above described are known to the Tuscan peasants under the name *Giaggiolo*, and when gathered from uncultivated plants the roots are mixed indiscriminately, the greater part then consisting of *I. germanica* and *I. pallida*, which are the most common.

The cultivation of the iris is an important industry in Italy, and the following excellent account of it will be found in the *Perfumery and Essential Oil Record*, 1922, 270 :—

"The *Iris pallida*, from which the (bulk of the) orris root of commerce is obtained, is grown in the districts surrounding Florence and Siena, in Tuscany. The dry, sun-baked Florentine hills seem peculiarly adapted for the cultivation of the iris, where other plants would be much less remunerative. Comparatively unimportant plantations of iris are scattered over northern Italy, particularly in Verona. The most renowned district for the cultivation of iris is that of which the village of San Polo is the centre. Here the iris represents a source of wealth on a level with the olives and wine for which Tuscany is justly world-famous, for it is precisely in this district that the famous Lucca olive oil, and the even more renowned Chianti wine are obtained. The farmers in San Polo sell their orris root to merchants in Florence, Milan, and Leghorn, who send it to France, England and Germany. It may be said that practically every farmer in San Polo grows iris as one of his crops, and from it he obtains the

flowers, bulbs, and roots. The bulbs arise from the 'eyes' that develop in the root, and vary in number, according to whether the plant is a two-year-old or three-year-old plant. They are used exclusively for reproduction, and for this purpose they are removed from the root in such a way as to leave a part of the root still adhering to them, as otherwise they are useless. The flowers are sold for ornamental purposes; the seeds do not reach maturity, and after cutting the flowers the root undergoes more rapid development and becomes richer in its aromatic principle. In San Polo the fields given over to iris have a southern aspect to ensure the greatest amount of sunshine. As soon as the previous crop is cleared off, the ground is harrowed and then levelled off. By the middle of September the bulbs are ready for planting. A man digs small trenches about 4 inches deep and 12 inches apart; he is followed by a boy who plants the bulbs about 10 inches apart in the trenches, and great care must be taken in this operation to see that the root adhering to the bulb is at the bottom of the trench. The bulbs are covered by the soil thrown up when the next trench is dug. The bulbs used are those gathered in the previous May or June, and about 80,000 are required for each acre of ground. A man and boy can plant about 6,000 per day, working in the above manner. No particular manure is required. Phosphates have been tried without success; it was found that larger leaves only were obtained, whilst dung gives rise to rot. On the other hand, previous crops—especially lupinella—are sometimes dug in and act as manure, whilst this operation also serves to render the soil free from weeds and better adapted for the development of the rhizome. The harvest is gathered in June and August, when the season is dry and the roots are well developed. The plant is taken up, and the rhizome is separated from the bulbs and freed from the roots. The bulbs are laid out in the open, with a covering of leaves over them, in preparation for their planting in the next season. The rhizomes are immersed in clear water to free them from adhering earthy matter, and following this they are decorticated. This operation is called *mondatura* locally, and is performed by women provided with small curved knives. Decortication by machinery has been attempted, but owing to the great irregularity in shape of the rhizomes, success has not been achieved so far. The machine consisted of a sharp circular knife, against which the peasant girl places the rhizome to be decorticated. To any one acquainted with the work it will be evident that by this means proper decortication can only be

obtained with great waste of valuable rhizome, whilst economy can only be effected at the expense of incomplete removal of the cortex, so that the operation is done by hand. The decorticated rhizomes are again cleaned in water, and then exposed on straw mats to dry in the sun. They are occasionally turned, in order to expose different surfaces, and thus effect uniform drying. Desiccation is effected in artificially-warmed and well-ventilated chambers only when the weather is wet. It is customary to leave the rhizomes in the open during clear, calm nights, in order to make them whiter, the result (it is said) of the action of the morning dew. When perfectly dry the rhizomes are ready for sale. The labour required for the cultivation is comparatively little during the early stages; the planting of the bulbs and the attention given them do not absorb much labour, which at that time is well occupied in the production of olive oils, wine, etc. In the summer, when the vines and olives require little attention, the iris harvest and the subsequent cleaning and decorticating of the rhizomes absorbs practically all the locally available labour. In the Florentine hills, in which San Polo is situated, is produced by far the greater part of the total output of orris root. In an average season about 300 tons represent the San Polo production, an acre of land yielding about one ton. The rhizome is worked up for the various orris products in Milan, Grasse, London, etc., and also, before the war, in Germany. The manufacture is, however, chiefly centred in Grasse."

Fresh orris root has an earthy smell, but little or no aromatic odour. The characteristic odour, which closely resembles violets, develops during the drying process and is probably due to fermentation changes. The odour improves by keeping the root, and is usually at its best after about two years.

*Iris germanica* is cultivated in Kashmir. It is known in India by its Persian name *Bikh i-banafshah*, which means "violet root." Indian orris root does not, as a rule, have its bark removed, and is of much less odour value than European orris root.

Normally distilled oil of orris is a semisolid substance, usually known as concrete oil of orris. It consists of from 80 to 85 per cent. of myristic acid (sometimes even 95 per cent.), with a comparatively small amount of odorous constituents. Nine samples were found (*P. & E. O. R.*, 1917, 275) to have the characters given in the table on p. 535.

No. 1 was remarkable for its high melting point, and a solution in 16 parts of alcohol (90 per cent.) crystallised into a semisolid

# P E R F U M E R Y

|       | Melting point. | Acid value. | Saponification value. |
|-------|----------------|-------------|-----------------------|
| 1 . . | 50°            | 208.0       | —                     |
| 2 . . | 45°            | 188.6       | 208.7                 |
| 3 . . | 39°            | 203.8       | 207.8                 |
| 4 . . | 40°            | 156.7       | 173.6                 |
| 5 . . | 39°            | 182.6       | 198.3                 |
| 6 . . | 46°            | 217.6       | 244.4                 |
| 7 . . | 34°            | 118.8       | 174.8                 |
| 8 . . | 39°            | 207.5       | 212.1                 |
| 9 . . | 44°            | 183.3       | 208.7                 |

mass at about 20°. The other samples remained in solution at 15° in the same proportion of alcohol. No. 7 had a very low melting point and a very low acid value, the difference between the acid and saponification values being considerably greater than in the majority of cases.

Tiemann and Krüger (*Berichte*, 1893, 26, 2675) found the odorous constituents of the oil to consist mainly of the ketone, irone,  $C_{13}H_{20}O$  (*q.v.*). Schimmel & Co. (*Report*, April, 1907, 76) have identified in the oil the following bodies: furfurol, a terpene, decyl aldehyde, nonyl aldehyde, naphthalene, and a ketone of the formula  $C_{10}H_{18}O$ .

Langlais and Goby (*P. & E. O. R.*, 1924, 311) have isolated the following acids from concrete oil of orris: octylic, nonylic, decylic, undecylic, dodecylic, and tridecyllic.

The following fractions were obtained by distillation at 40 mm. :—

- (1) 150° to 151°, small quantity of liquid.
- (2) 162° to 163°, small quantity of liquid.
- (3) 174° to 175°, important quantity of solid.
- (4) 185° to 186°, small quantity of liquid.
- (5) 198° to 200°, important quantity of solid.
- (6) 210° to 212°, small quantity of solid.

The following is the account by the authors of their examination of these fractions :—

(1) The fraction distilling at 150° to 151° had a fatty smell, recalling that of perspiration. Redistilled under a pressure of 4 mm., it boiled at 110° to 111°, and at 237° to 238° under the normal atmospheric pressure (758 mm.); the boiling point corresponded to that of a saturated octylic acid. To verify this we

took the index of acidity : 1.2141 grams of the acid in alcoholic solution required for neutralisation, in the presence of phenolphthalein, 16.7 c.c. of semi-normal potash, showing the molecular weight to be (for a monobasic acid) 145.5. The calculated molecular weight of the saturated acid with 8 carbon atoms is 144.

Finally, we prepared the anilide by heating for two hours on a sand bath with a slight excess of freshly distilled pure aniline. After purification and repeated crystallisation from weak alcohol, the melting point was found to be  $51^{\circ}$ . The recent work of Asano (*Bull. Soc. Chim.*, 1922, **32**, 1710) indicated  $51.5^{\circ}$  as the melting point of octylic anilide.

Determination of the silver salt : Weight of substance, 0.755 gram ; weight of silver, 0.3601 gram ; calculated for  $C_8H_{15}O_2Ag = 251$ , found 251.7. These results confirm the presence of caprylic acid.

(2) Fraction  $162^{\circ}$  to  $163^{\circ}$ . Redistilled, it boiled at  $253^{\circ}$  to  $255^{\circ}$  at atmospheric pressure, and at  $124^{\circ}$  to  $125^{\circ}$  under a pressure of 4 mm. The molecular weight calculated initially from the index of neutralisation : Weight of substance, 0.890 gram, neutralising 11.2 c.c. of semi-normal potash = 159 (calculated for  $C_9H_{18}O_2 = 158$ ).

Saponified with ethyl alcohol and sulphuric acid the ester had a very pronounced odour of rum.

The anilide melted sharply at  $57^{\circ}$ , thus pointing to a nonylic acid, i.e., pelargonic acid.

It has always been believed that pelargonic acid existed in oil of geranium (Pless, *Liebig's Annalen*, 1846, **59**, 54) from *Pelargonium odoratissimum* and *P. roseum* ; hence the name—but Messrs. Schimmel & Co. (*Bericht*, April, 1894) have only identified in this oil an unsaturated acid—tiglic acid.

(3) The fraction  $174^{\circ}$  to  $175^{\circ}$  forms an important part of the fractionation. The boiling point is from  $138^{\circ}$  to  $139^{\circ}$  under 4 mm. pressure, and from  $268^{\circ}$  to  $270^{\circ}$  at normal pressure. After a first crystallisation in weak alcohol and cooling, we have made the barium salt, which is deposited in the crystalline state from its boiling aqueous solution. Converted into the sodium salt by sodium carbonate and liberated by dilute sulphuric acid, the acid melted at  $31^{\circ}$ . The molecular weight found was 172.3 (calculated for  $C_{10}H_{20}O_2 = 172$ ). The anilide recrystallised thrice from 70 per cent. alcohol melted at  $65.5^{\circ}$ . The ethylic ester under 4 mm. boiled at  $104^{\circ}$ . The specific gravity at  $28^{\circ}$  was 0.859.

Ester index : Substance, 1.505 grains, semi-normal potash

15 c.c. gave 279; calculated for  $C_9H_{19}COOC_2H_5 = 280$ . These results clearly point to decylic (capric) acid.

One would naturally expect to find these two acids,  $C_9$ ,  $C_{10}$ , because the researches of *Schimmel & Co.* (*Bull. Sem.*, April, 1907) have shown the existence in oil of orris of their two aldehydes---nonylic and decylic.

(4) We have seen that the preceding fraction is solid at a temperature about  $28^\circ$ . The higher fraction,  $185^\circ$  to  $186^\circ$ , is completely liquid, which presumes the presence of an acid with an unequal number of carbon atoms; for according to the rule of melting points we find in homologous series (especially with the aliphatic acids) that the higher terms with unequal carbon atoms have lower melting points than those of the terms containing one less atom of carbon, so that whilst the boiling point rises progressively, the melting point of successive terms rises and falls alternately.

Clearly we have here undecylic acid, of which the constants found are as follows: boiling point under 4 mm.,  $145^\circ$  to  $146^\circ$ ; under normal pressure,  $280^\circ$ .

As the melting point observed,  $27^\circ$ , was slightly below that found in literature, we have verified that the acid does not possess a double ethylenic linking! When dissolved in sodium carbonate, the acid does not decolourise potassium permanganate. Bromine dissolved in carbon bisulphide is not decolourised, and no bromide is formed. The iodine value is *nil*.

Molecular weight: Substance, 1.358 grams; semi-normal potash 14.8 c.c. gave 184—calculated for  $C_{11}H_{22}O_2 = 186$ .

The anilide melts at  $71^\circ$ . Asano found  $68^\circ$ , and Robertson (*Bull. Soc. Chim.*, 1920, 28, 132)  $71^\circ$ .

Determination of silver salt: Found 291, calculated 293.

(5) The fraction  $198^\circ$  to  $200^\circ$  is crystalline, and as important as the capric acid fraction. Redistilled under 4 mm. it passed over at  $153^\circ$  to  $154^\circ$ . Purified by recrystallisation from 70 per cent. alcohol, the acid melted sharply at  $43.5^\circ$ . The molecular weight is: Substance, 1.0964 grams, which neutralised 11 c.c. of semi-normal potash, giving 199.3—calculated for  $C_{12}H_{24}O_2 = 200$ . The anilide very easily crystallised from 70 per cent. alcohol, and melted at  $75.5^\circ$  (Asano,  $75^\circ$ ), thus proving normal dodecylic acid, that is to say, lauric acid.

(6) The fraction  $210^\circ$  to  $212^\circ$  came over immediately before the myristic acid— $C_{14}$ —and is composed of tridecylic acid, melting at  $39^\circ$  (stated to melt at  $40.5^\circ$ ). This difference is undoubtedly

due to the small amount of material at our disposal, which made a more complete purification impossible. The molecular weight found was 215—calculated for  $C_{13}H_{26}O_2 = 214$ .

The anilide, after three crystallisations from 70 per cent. alcohol, melted sharply at  $81.5^\circ$  (Robertson has found  $80^\circ$ ).

(7) Finally, the mother-liquors of the  $C_6$  fractions, much diluted and cooled, threw down a slight precipitate which, recrystallised from water, melted at  $121^\circ$ . Mixed with benzoic acid the melting point was not lowered, and we think it to be benzoic acid.

Liquid oil of orris—that is, the oil almost entirely freed from its myristic acid, and therefore highly concentrated—is to-day a well-recognised commercial article. Its characters are as follows:—

|                  |           |                              |
|------------------|-----------|------------------------------|
| Specific gravity | . . . . . | 0.930–0.942                  |
| Optical rotation | . . . . . | + $14^\circ$ to + $30^\circ$ |
| Refractive index | . . . . . | about 1.4950                 |
| Acid value       | . . . . . | 1–10                         |
| Ester value      | . . . . . | 20–40                        |

It is soluble in 1 to 1.5 volume of 80 per cent. alcohol.

This liquid oil, which is a very expensive and a very beautiful preparation, must not be confused with a so-called “liquid orris” which is merely the product of distillation of cedar wood oil, or some similar oil, with orris root, or probably more frequently a direct mixture of the two oils. Such oils usually have a specific gravity over 0.940, and are laevorotatory up to  $-30^\circ$ .

**OSMORHIZA LONGISTYLIS.**—The root of this plant, which belongs to the natural order *Umbellifera*, and which is known in North America as “sweet cicely,” has a marked odour of aniseed and fennel. The root yields about 0.6 per cent. of essential oil which has been examined by Eberhart (*Pharm. Rundsch. New York*, 1887, 5, 149). He found it to have a specific gravity 1.0114 at  $10^\circ$ ; congealing point,  $10^\circ$  to  $12^\circ$ ; and melting point,  $16^\circ$ . It contains anethol as its principal constituent.

**OSYRIS OIL.**—A tree of this genus, which is probably *Osyris tenuifolia*, is known in East Africa as a “sandalwood” tree. Schimmel & Co. have examined the essential oil from the wood, which was obtained to the extent of 4.86 per cent. (*Bericht*, October, 1908, 111). It had the odour of a mixture of vetiver oil and gurjun balsam. Its specific gravity was 0.9477; optical rotation,  $-42^\circ 50'$ ; refractive index, 1.5219; ester value, 11.1; and ester value after acetylation, 72.8, corresponding with a content of sesquiterpene alcohol of 30.5 per cent. Two oils,



## P E R F U M E R Y

described as African sandalwood oil, but whose botanical origin is unknown, have also been described by Haensel (*Chem. Zentral.*, 1906, ii., 1496). They had the following characters :—

|                                   |         |    |          |
|-----------------------------------|---------|----|----------|
| Specific gravity at 20° . . . . . | 0.9589  | .. | 0.9630   |
| Optical rotation . . . . .        | — 40.6° | .. | — 60.96° |
| Ester value . . . . .             | 17.9    | .. | 8.1      |
| Ester value after acetylation     | 88.3    | .. | 68.6     |

These were probably osyris oils. A sesquiterpene and a sesquiterpene alcohol were found present in the oils.

**OTTO OF ROSE.**—See “Rose.”

**PÆONOL.**—This body is a ketone of the formula  $C_9H_{10}O_3$ , found in the essential oil of *Pæonia Moutan*. It is *para*-methoxy-*ortho*-hydroxyphenyl ketone. It has been prepared synthetically by Hoesch (*Berichte*, 1915, 48, 1122).

**PALMAROSA OIL.**—See “Gingergrass Oil.”

**PALO BALSAMA.**—See “Bulnesia Sarmienti.”

**PALO BLANCO.**—The tree *Chione glabra*, belonging to the natural order *Rubiaceæ*, is known in Porto Rico as *Palo blanco*, and in Grenada as *violette*, on account of the aromatic odour of its flowers. The bark yields an oil having a somewhat disagreeable odour, which contains hydroxy-acetophenone. The flowers do not appear to be used commercially for perfumery purposes.

**PAOLO AMASELLO.**—The wood of the tree known in Brazil as *Paolo amasello*, of unknown botanical origin, yields an essential oil to the extent of 0.41 per cent. It has been examined by Roure-Bertrand Fils (*Bulletin*, October, 1910, 41). It has an odour resembling that of linaloe oil. It has a specific gravity 0.8892; optical rotation, — 5° 54'. It consists mainly of free alcohols, with 8 per cent. of esters calculated as linalyl acetate.

**PARACOTO BARK OIL.**—The bark of an unknown species belonging to the natural order *Monimiaceæ*, known in Bolivia as paracoto bark, yields an essential oil of specific gravity about 0.927, and optical rotation — 2°. According to Jobst and Hesse (*Annalen*, 1879, 199, 75), it contains two hydrocarbons, but Wallach and Rheindorff (*Annalen*, 1892, 271, 300) have shown that the earlier work was not reliable, and have proved the presence of cadinene and methyl-eugenol in the oil.

**Para - METHYL - ACETOPHENONE.** — See “Methyl-aetophenone.”

**Para - METHYL - HYDROCINNAMIC ALDEHYDE.** — This body is a homologue of hydrocinnamic aldehyde, an aldehyde which exists naturally in the essential oil of cinnamon bark. It has been prepared synthetically, and has a powerful odour of the lily and lilac type.

**PATCHOULI.**—Oil of patchouli is distilled from the leaves of several species of *Pogostemon*, of which *P. patchouli* is the principal. E. M. Holmes (*P. & E. O. R.*, 1913, 369) gives the following details of the botany of the plants :—

Patchouli has long been known and cultivated in India and the Straits Settlements and various islands of the Indian Ocean, so long, indeed, that its original country was lost sight of until quite recently. The first notice of its appearance in European commerce appears to be that given by J. J. Virey in 1826 (*Jour. de Pharm.*, 1826, xii., 61), who describes it as having been brought from the Isle of Bourbon, where it was evidently cultivated, the flowers being unknown, and it was doubtfully referred to as *Plectranthus graveolens*, a native of New Holland. It was spoken of by Virey as an insectifuge for clothes and shawls. The first notice of a sale of the leaves in this country is an account given by Dr. Pereira (*Pharm. Jour.*, 1, iv., 808) of forty-six cases put up for sale at Garraway's Coffee House on June 27th, 1844, by Mr. Ellis, a drug broker of Fenchurch Street. It was recognised by Pereira as an East Indian product, for he says that it had been introduced into the Botanic Gardens at Calcutta from Penang, but that up to 1841 it had not flowered there. Its introduction into Europe is accounted for by a writer in the *Gardener's Chronicle* (1849, 645), by the fact that a few years previously real Indian shawls bore an extravagant price, and purchasers could always distinguish them by their odour of patchouli. The French manufacturers, having discovered the secret of their odour, imported the dried leaves to perfume articles of their own make and thus palm off their homespun shawls for real Indian. The true patchouli plant was first described and illustrated in 1845 by Dr. Pelletier-Sautelet (*Mem. de la Soc. Roy. des Sciences d'Orleans*, v., 6), the plant having flowered at Orleans in February of that year, and the description and figure of the plant were copied into the *Pharmaceutical Journal* (1849, I., viii., 574). In the spring of 1849 the plant flowered at Kew, and another illustration of the plant, but not quite so character-

istic, was published in Hooker's *Journal of Botany* (1849, 329, Plate XI). The plant was supposed by Pelletier-Sautelet to be hitherto undescribed, in consequence of its not having previously been seen in flower, and he named it *Pogostemon patchouli*. Its native country remained unknown until 1896, when E. M. Holmes was able to identify it as a wild plant of the Philippine Islands which had been described by Blanco under the name *Mentha cablin* in the "Flore de Filipinos" in 1837.

The true patchouli plant, *Pogostemon patchouli*, is known in the Straits Settlements as *Dhalum wangi* or *Tilam wangi* ("sweet patchouli"). It is cultivated principally by the Chinese in the Straits Settlements, Penang, Singapore, and the Wellesley Province. The plant rarely, if ever, flowers there. *Pogostemon Heyneanus* is the plant which is cultivated in Java, and there flowers freely. It is the source of Javan patchouli oil.

Patchouli leaves are often grossly adulterated by admixture with other leaves. Amongst the commonest of such leaves are those of *Ocimum basilicum* var. *pilosum*, known as *Ruku* by the Malays. The leaves of *Urena lobata* var. *sinuata*, a weed growing in the cocoanut plantations, is also commonly used. This is the plant known as *Perpulut* by the Malays. *Hyptis suaveolens*, *Plectranthus fruticosus*, *Lavatera olbia*, and *Paronia Weldenii* are also used as adulterants.

The Sekais of Batang-Padang call the patchouli plant *Boon kalif*, and the Malay name is *Poko nilam*, the leaves being called *Down nilam*.

In the Malay peninsula patchouli is both a wild and a cultivated crop. The plant is a soft-leaved herb from 2 to 3 feet in height, much branched, with square stems. It is frequently planted on newly cleared ground among the felled logs. Being slightly shaded, it flourishes in such ground. The best method of propagation is by cuttings of young shoots. These are cut about 3 inches long, care being taken to cut them just below a joint. It can be grown as a catch crop in young rubber or cocoanut clearings. The first crop can be gathered six months after the planting, and afterwards twice a year. In Perak it is usual to take only three crops, and then to replant. The leaves, when cut, may be dried in the sun, but it is better to dry them in the shade by spreading them out in a cool and airy shed. After about a week they are dry enough to be packed in bales. Most of the leaves are exported to Marseilles and New York.

Patchouli was at one time cultivated to a considerable extent

## P E R F U M E R Y

in Johore. The industry, however, declined on account of more attractive crops being available, but within the last two or three years efforts have been made to revive it.

When cultivated on suitable land, three cuttings may be taken before replanting becomes necessary. But the land requires a rest, for subsequent plantings, if cultivated without such rest, give very poor crops. The dried plants are distilled in ordinary steam stills, and the oil is of quite fair average quality.

A picul (133 lb.) of leaves yields from 24 to 30 oz. of oil, or if the leaves are free from stalk, about double this quantity. There is added to the stills, in some distilleries about 25 per cent. of wild patchouli, known as *Tilam outan*, a species of *Pogostemon* not yet determined.

Two species of *Microtæna* are also distilled for so-called patchouli oil, which, however, is not found in European markets. These are *Microtæna cymosa*, which is cultivated in Assam, and *M. robusta*, which is distilled in China.

A. W. K. de Jong has carried out an investigation to assist the distillers in knowing the best conditions for gathering and distilling the leaves. He found that the essential oil resides principally in the three top pairs of leaves, that is, the most recently developed ones, and he recommends that the plants should be cut

### *Singapore Oils*

|                          | Fresh leaves. | Dry leaves. | Fermented leaves. |
|--------------------------|---------------|-------------|-------------------|
| Specific gravity . . . . | 0.9655        | 0.9587      | 0.9628            |
| Optical rotation . . . . | — 51° 18'     | — 50° 58'   | — 52° 23'         |
| Refractive index . . . . | 1.5082        | 1.5077      | 1.5078            |
| Ester value . . . . .    | 2.0           | 1.1         | 1.5               |

### *Java Oils*

|                          | Fresh leaves. | Fresh leaves. | Dry leaves. | Slightly fermented leaves. | Strongly fermented leaves. |
|--------------------------|---------------|---------------|-------------|----------------------------|----------------------------|
| Specific gravity . . . . | 0.9344        | 0.945         | 0.9168      | 0.9229                     | 0.9210                     |
| Refractive index . . . . | 1.5005        | 1.5048        | 1.5003      | 1.5006                     | 1.5021                     |
| Optical rotation . . . . | — 15° 20'     | — 15° 20'     | + 3° 15'    | + 2° 32'                   | — 0° 26'                   |
| Ester value . . . . .    | 9.9           | 5.8           | 6.1         | 4.9                        | 5.0                        |

## P E R F U M E R Y

directly five pairs of leaves have developed. In the case of Singapore oil, he found that there was very little difference between oils distilled from fresh, dry, and fermented leaves ; but in the case of Java oils the treatment of the leaves has a considerable influence on the characters of the oils. The tables on p. 542 illustrate the influence of such treatment.

For general purposes three different types of patchouli oil may be recognised as commercial articles : (1) oils distilled in Europe from dried leaves ; (2) oils distilled in Singapore ; (3) oil distilled from Java leaves. The oils distilled in Europe from the true patchouli leaves vary in colour from a yellowish or greenish-brown to a dark brown. The oil is very viscid, and crystals often separate in the oil on standing. The European oil has the following characters :—

|                            |                |
|----------------------------|----------------|
| Specific gravity . . . . . | 0.966–0.995    |
| Optical rotation . . . . . | — 47° to — 71° |
| Refractive index . . . . . | 1.5070–1.5125  |
| Ester value . . . . .      | 2–12           |

Oils distilled in Singapore are usually paler in colour than the oils distilled in Europe, and their odour is less intense. These oils have the following characters :—

|                            |                |
|----------------------------|----------------|
| Specific gravity . . . . . | 0.960–0.985    |
| Optical rotation . . . . . | — 45° to — 65° |
| Refractive index . . . . . | 1.5080–1.5120  |
| Ester value . . . . .      | 1.5–7          |

Java patchouli oils distilled in Java, known as “Dilam oil” to distinguish them from the oil from *Pogostemon patchouli*, have the following characters :—

|                            |               |
|----------------------------|---------------|
| Specific gravity . . . . . | 0.925–0.935   |
| Optical rotation . . . . . | + 3° to — 33° |
| Ester value . . . . .      | 6–20          |
| Refractive index . . . . . | 1.5000–1.5080 |

*Roure-Bertrand Fils* (*Bulletin*, April, 1910, 18) have examined the oil obtained from (a) the leaves, (b) the branches of patchouli grown in Sumatra, and give the following figures for them :—

|                                | Leaf oil. | Branch oil. |
|--------------------------------|-----------|-------------|
| Specific gravity . . . . .     | 0.9689    | 0.9739      |
| Optical rotation . . . . .     | — 52° 4'  | — 54° 8'    |
| Acid number . . . . .          | 1.2       | 8.7         |
| Ester number . . . . .         | 6.7       | 1.3         |
| Ester number after acetylation | 26.13     |             |

# PERFUMERY

| Origin.   | Specific gravity at 15°. | Optical rotation. | Solubility.   | Saponification value |                    |
|---|--------------------------|-------------------|---|----------------------|--------------------|
|   |                          |                   |   | Of the oil.          | Of acetylated oil. |
| Singapore variety cultivated in Java. Fresh plants    | 0.9662                   | — 52° 2'          | 0.5 vol of 90 per cent alcohol, subsequently a cloudiness, soluble in 5 vols and over.        | 2.7                  | 20.7               |
| Singapore variety Dried plants.                       | 0.9677                   | — 51° 32'         | 8 vols of 90 per cent. alcohol and over   | 0                    | 12.5               |
| Javan variety Fresh Plants } First distillation.      | 0.9112                   | — 0° 52'          | 8.5 vols of 90 per cent. alcohol and over.  | 4.1                  | 33.4               |
| Javán variety Fresh plants } Second distillation.     | 0.9457                   | — 15° 18'         | 0.5 vol of 90 per cent. alcohol, then a cloudiness which is redissolved in 3.5 vols and over. | 2.7                  | 43.8               |
| Javan variety. Dried plants.                          | 0.9174                   | + 3° 24'          | 8 vols of 90 per cent. alcohol and over   | 3.4                  | 13.9               |
| Javan variety. Plants slightly fermented.             | 0.9217                   | + 2° 40'          | 12 vols of 90 per cent. alcohol slightly cloudy.  | 2.7                  | 34.1               |
| Javan variety. Plants strongly fermented.             | 0.9236                   | — 0° 08'          | 8 vols of 90 per cent alcohol and over  | 2.1                  | 32.1               |
| Singapore variety. Dried plants. Our own distillation | 0.9888                   | — 61° 04'         | 0.5 vol of 90 per cent alcohol and over 1 vol of 85 per cent. alcohol and over.               | 3.5                  | 24.3               |

## P E R F U M E R Y

*Roure-Bertrand Fils* have also distilled the oil in France, from Java leaves, and found it to have characters differing from those the Java distilled oils usually have. They were as follows :—

|  |          |
|--|----------|
| Specific gravity . . . . .             | 0.9564   |
| Optical rotation . . . . .             | — 28° 8' |
| Saponification value . . . . .         | 6.3      |
| Saponification value after acetylation | 40.4     |

A sample of oil distilled from leaves from Perak has been examined at the Imperial Institute and found to have a specific gravity 0.9595; optical rotation, — 43° 51'; and refractive index, 1.5063.

*Roure-Bertrand Fils* (*Bulletin*, October, 1908, 22) give the characters of Java oils distilled from the Javan and Singapore varieties of leaves shown in the table on p. 544, and compare them with a French distillate of Singapore leaves.

According to the *Bulletin of the Imperial Institute* (xii, No. 3, 1924), Seychelles patchouli oil resembles the Singapore oil in its constants. Four samples were examined, which had the following characters .—

|  | No. 1.  | No. 2.   | No. 3.                     | No. 4.                     |
|--|---|--|----------------------------|----------------------------|
| Sp. gr. at 15/15° . . . . .                      | 0.9560  | 0.9484   | 0.969                      | 0.940                      |
| Optical rotation $\alpha_D^{20^\circ}$ . . . . . | — 47.56   | — 51.8   | *                          | *                          |
| Refractive index $n_D^{20^\circ}$ . . . . .      | 1.5075  | 1.5075   | 1.509                      | 1.502                      |
| Acid value . . . . .                             | 2.0   | 1.3  | †                          | 3.2                        |
| Ester value . . . . .                            | 3.0   | <i>Nil.</i>  | †                          | 5.3                        |
| Solubility in 90 per cent.<br>alcohol at 15°.    | Not<br>entirely<br>soluble<br>even in<br>11 vols. | Not<br>com-<br>pletely<br>soluble<br>even in<br>12 vols. | Soluble<br>in 0.5<br>vols. | Soluble<br>in 6.5<br>vols. |

The following observations were made on the four oils :—

No. 1. Somewhat cloudy, owing to the presence of moisture. The clear filtered oil, which was greenish-brown, was rather more limpid. The oil had a good though not very intense aroma, and was of fairly satisfactory colour. Its constants resembled those of imported Singapore oils, but the solubility and the specific gravity were rather low.

No. 2. This consisted of clear greenish-yellow patchouli oil,

- \* Undeterminable owing to dark colour of the oil.
- † Not determined.

with the characteristic odour of that product. The results of examination of the oil are given in the table above. The oil was superior in aroma and colour to sample No. 1, but otherwise it resembled the latter oil except as regards specific gravity, which is somewhat lower. In this respect it more nearly approached the patchouli oil which is obtained in Java. Patchouli oil of this quality would be readily saleable in the United Kingdom.

No. 3 consisted of patchouli containing a small amount of dirt and moisture, which rendered it cloudy. The clear filtered oil was greenish-brown. The oil possessed a peculiar subsidiary odour in addition to the intense characteristic odour of patchouli. The results of the examination of the oil at the Imperial Institute are shown in the above table. The oil was unusually soluble in 90 per cent. alcohol for a genuine patchouli oil, and its odour was quite distinct from that of the previous samples from Seychelles examined at the Imperial Institute. Importers and manufacturers who were consulted regarded the sample as much inferior to the best commercial grades of patchouli oil. The general view expressed was that, owing to its unusual odour and dark colour, the oil would be difficult to dispose of in this country, and that in any case it would have to be offered at a price considerably lower than that of commercial Singapore or Penang patchouli oils.

No. 4. This oil had been obtained by the distillation of dry leaves, and it was desired to ascertain its quality in comparison with that of oil distilled from fresh leaves. The sample, which was described as "Essence de Patchouli Penang, Feuilles seches," consisted of a clear green oil, which had the characteristic odour of patchouli, but was rather more limpid than the ordinary patchouli oil of commerce. The constants of this oil, as determined at the Imperial Institute, are given in the above table. This oil, prepared from dry leaves, was much less soluble in alcohol than the oil distilled from fresh leaves (No. 3), but was considerably paler and of better odour. It possessed to some extent the peculiar subsidiary odour noticed in sample No. 3, and this would render it of lower commercial value than Penang and Singapore oils.

The oil contains a sesquiterpene alcohol,  $C_{15}H_{26}O$ , which is known as "patchouli alcohol"; this body was originally termed patchouli camphor. It is a crystalline substance melting at  $56^{\circ}$ , and having a specific rotation  $-118^{\circ}$  in the melted condition. There is also present a sesquiterpene which has been termed



**patchoulene.** It has a specific gravity 0.933 at 15°; optical rotation,  $-36^{\circ} 52'$ ; and boils at 255°. According to *Schimmel & Co. (Report, April, 1904, 68)* patchouli oil contains about 97 per cent. of bodies of no value for odour purposes. They have detected the following substances in the oil; benzaldehyde, eugenol, cinnamic aldehyde, a terpene alcohol of rose odour, a ketone with a caraway odour, and a basic substance of stupefying odour (see also *P. & E. O. R.*, 1924, 285).

**PELEA MADAGASCARICA, OIL OF.**—The leaves and fruits of *Pelea Madagascariensis* yield from 4 to 5 per cent. of essential oil, having a powerful odour of aniseed. It contains anisic aldehyde and anethol, and has a specific gravity 0.953; optical rotation,  $+32^{\circ}$ ; and refractive index, 1.5147.

**PE-MOU, OIL OF.**—Gardies (*La Parfumerie Moderne*, 1923, 110) has examined the essential oil distilled from the wood of *Fokienia Hodginsii*, a Chinese conifer whose wood is valued for making coffins which resist decay, and joss sticks and similar substances for ceremonial burning. It has a very sweet odour, recalling cedarwood and terpineol. Its characters are as follows: specific gravity, 0.913; optical rotation,  $+13^{\circ}$ ; refractive index, 1.4937; esters, 8.1 per cent.; and free alcohols, 41.4 per cent.

**PENNYROYAL OIL.**—The ordinary pennyroyal oil of commerce is derived from the leaves and other green parts of the plant *Mentha pulegium*. The American pennyroyal oil is distilled from an entirely different plant, *Hedeoma pulegioides*. E. M. Holmes (*P. & E. O. R.*, 1911, 254) gives the following account of the true pennyroyal and allied species:—

Two forms of the plant are met with in this country, the commonest form having weak, prostrate stems, which root at the joints and form a dense green turf. This is named var. *decumbens*. The flowering stems are sparingly produced, and often lie prostrate on the leafy cushions of the plant. The other form, known as var. *erecta*, has stouter upright flowering stems, which bud off lateral stolons or prostrate branches near the base. These root sparingly, forming new plants, which give rise to upright flowering stems during the ensuing year. This is much rarer as a wild plant, but is the best for cultivation, as it can be reaped and tied up into bundles more readily. The stems are usually 6 to 9 inches long, but under favourable conditions, such as a moist soil and a warm climate like that of Devon and Cornwall, will grow to 15 or 18 inches. There are several other varieties of this

## P E R F U M E R Y

plant found on the Continent. One variety, *eriantha*, with hairy flowers, occurs at Biarritz, and a similar form has been found near Falmouth in this country. Another, in which the whole plant is hairy, is found in Sicily, and is named var. *tomentosa*; and a third, covered with rather stiff hairs, named var. *tomentella*, is found near Montpellier and in Hungary. A fourth, with small leaves, occurring in eastern Europe, is named var. *thymifolia*, and on the steppes of southern Russia a hairless form with smaller leaves and flowers has been described as a variety, but as it is an annual plant it has probably the right to specific rank, and should be called *Mentha micrantha*. It has been called *Pulegium micranthum*. Of these varieties it is uncertain which are used on the Continent as sources of the oil, but the plant used in Spain, so far as can be judged, belongs to the variety *eriantha*. The Russian oil is stated to be derived from *Mentha micrantha*; the European oil is distilled in the Spanish provinces Huelva and Cadiz, in the south of France, Algeria, and to a small extent in Turkey. The oil is of a yellow to red-yellow colour, sometimes distinctly fluorescent. It has the following characters:—

|                  |           |                      |
|------------------|-----------|----------------------|
| Specific gravity | . . . . . | 0.930–0.952          |
| Optical rotation | . . . . . | + 15° to + 25°       |
| Refractive index | . . . . . | 1.4820–1.4865        |
| Pulegone         | . . . . . | From 80–94 per cent. |

The principal constituent of the oil is the ketone pulegone,  $C_{10}H_{16}O$ . Terpenes, menthol, and menthone are also present.

The Russian oil, although distilled from a different plant, has substantially the same characters.

The American plant, *Hedcoma pulegioides*, is found from the Atlantic States to the Rocky Mountains, and as its preparation requires only simple apparatus it is distilled at numerous small factories. The bulk of the oil is said to be distilled in North Carolina, and particularly in the southern and eastern parts of Ohio, and in Tennessee. The American oil has characters very similar to those of the European oil, but the specific gravity usually lies between 0.925 and 0.940, and the optical rotation, between + 18° and + 35°. Its principal constituent is pulegone, but small quantities of two other ketones are said to be present, one of which is probably menthone, and the other has been named hedcomol by its discoverer, Kremer. This body has the formula  $C_{10}H_{18}O$ , boils at 170°, and yields an oxime melting at 41° to 43°.

Barrowcliff (*Jour. Chem. Soc.*, 1907, **91**, 875) has examined the

oil, and found present a phenol, pinene, limonene, dipentene, methyleyclohexanone, pulegone, menthone, isomenthone, a sesquiterpene alcohol, and esters of formic, acetic, octoic, decylic and salicylic acids, and also of a dibasic acid,  $C_8H_{14}O_4$ , together with small quantities of free acids. He does not find any ketone corresponding with Kremer's hedeomol.

**PENTINE CARBONATES.**—See “Heptine Carbonates.”

**PEPPERMINT OIL.**—This oil is produced in many countries, the bulk of the world's supplies being distilled in the United States and Japan. English oil, however, although produced on a comparatively small scale, is the most highly appreciated, and commands a very high price. France, Italy, Russia, Germany and other countries also distil a certain amount of the oil. The oil distilled in the United States is obtained from the herb *Mentha piperita* in several of its varieties or forms, whilst the much inferior Japanese oil is distilled from *Mentha arvensis*. The Japanese oil alone is so rich in menthol that this body easily crystallises from the oil, and the world's supply of menthol is obtained from this source. The residual oil even then still contains from 40 to 50 per cent. of menthol, or even more, and is sold as Japanese dementholised peppermint oil, which is the Japanese peppermint oil of commerce.

The conditions under which the plants are grown have considerable influence on the character of the resulting peppermint oil. Apart from this, the plants used are not identical in characters in the different localities.

In discussing the English peppermint plant, it will be necessary to deal at the same time with the French plants, as some confusion has been created in regard to the relationships of these peppermint varieties. The well-known botanists A. and E. G. Camus (*Bulletin Roure-Bertrand Fils*, October, 1911, 3), as the result of a critical examination of the cultivated peppermints of France, came to the conclusion that *Mentha piperita* was not to be represented as a separate species, but as a hybrid between *Mentha viridis* and *Mentha aquatica*. They also found that two well-defined varieties were cultivated in the south of France, which they named *Mentha piperita officinalis* var. *pallescens*, and *Mentha piperita officinalis* var. *rubescens*. Of these they considered the former as identical with the so-called white mint, and the latter as identical with the so-called black mint cultivated in England.

E. M. Holmes (*P. & E. O. R.*, 1912, 10) has made a careful examination of this work, and points out that the varieties described by Camus do not correspond with the *blanche* and *noire* cultivated forms described by the well-known authorities Planchon and Collin, nor with the white and black cultivated peppermints of this country. The forms described by Planchon and Collin have, according to these eminent authorities, the following diagnostic characters:—

*Blanche*.—Stem as well as the leaves green; leaves scarcely toothed; flowers nearly white.

*Noire*.—Leaves longer, purplish, distinctly toothed; flowers dull red, not expanding freely. This form gives a larger yield of oil, but the odour is not so good as in the *blanche* form.

The two forms characterised and illustrated by MM. Camus are described as follows:—

(1) *Mentha piperita* var. *officinalis* Sole, form *pallescens*.—Stems green as well as the leaves; calyx almost entirely glabrous, the calyx teeth furnished with hairs, which are more numerous near the apex. Inflorescence forming spikes more or less interrupted at the base, longer upon the terminal branches.

(2) *Mentha piperita* var. *officinalis* Sole, form *rubescens*.—Stems tinted more or less with purple as well as the leaves; calyx glabrous at the base, glabrescent at the summit, the teeth furnished with usually rather more numerous hairs than in the form *pallescens*. Inflorescence of the lateral branches usually capitate.

These latter forms are evidently much more nearly allied in the form of the inflorescence to *M. viridis*. This is so much the case that, if *Mentha piperita* is, as French botanists maintain, a hybrid between *Mentha aquatica* and *Mentha viridis*, then these French varieties evidently have more of the *M. viridis* parentage in their composition than the English forms *vulgaris* and *officinalis*, which exhibit much more of the *M. aquatica* in their constitution, since in the English species the prominent character of the inflorescence is that it is oblong and obtuse, i.e., of the capitate character rather than of the tapering, spike-like character of *M. viridis*, so characteristic of the two French varieties.

It may be noted in passing that in these two French varieties the anthers are represented as included in the tube of the corolla, whilst in both the assumed parents, *M. aquatica* and *M. viridis*, of which illustrations are given by MM. Camus, the anthers are represented as exserted. In any case, it can hardly be expected that the French forms *pallescens* and *rubescens*, with more of the

parentage of *M. viridis*, are likely to yield an essential oil identical with that obtained from the English forms, in which the parentage of *Mentha aquatica* seems to preponderate.

As MM. Camus remark, "The climate has probably less influence on the character of the oil than the choice of varieties and the mode of cultivation."

M. Briquet, an authority on the genus *Mentha*, quoted by MM. Camus, recognises the following forms of *Mentha piperita* as occurring in France, most of which have an elongated inflorescence, passing in nearly all the varieties into a capitate inflorescence on the secondary axes:—

(1) Var. *officinalis*. With narrowly lanceolate or elliptic lanceolate leaves.

(2) Var. *durandoana*. Leaves oblong-elliptic, or sometimes ovate-oblong. Teeth of the leaves irregular, 3 to 5 mm. distant, directed forwards, acute, mucronate, and crenate. Calyx distinctly tubular, resembling that of *M. aquatica*.

(3) Var. *inarimensis*. Teeth of the leaves less pronounced. Calyx smaller, resembling that of *M. viridis*. Inflorescence spiked on the principal axes.

(4) Var. *globosiceps*. Inflorescence capitate on all the axes.

In all these varieties the plants are nearer to *M. viridis* than to *M. aquatica*, except in *M. globosiceps*, and in this variety the heads are apparently globose, and have not the oblong, obtuse character of the English peppermints. In no respects, therefore, can the French varieties of *Mentha piperita* be considered identical with those cultivated in Great Britain.

There is no doubt, whatever be the opinions of botanists as to whether or no the plant is entitled to specific rank, that the cultivated peppermint of this country is *Mentha piperita* var. *officinalis* in two forms, the white and the black, which are not identical with the forms described by Camus for the French mints, nor with the *blanche* and *noire* forms of Planchon and Collin. (See also *Conference Bulletin* No. 2, University of Wisconsin, 1922, for the nomenclature of peppermint types.)

The area under cultivation in England is comparatively small, and is confined to a few districts. The peppermint known as "Mitcham" indicates plants grown in Surrey, around Mitcham, Reigate, Wallington, Carshalton, Ewell, Dorking, Leatherhead, etc. In addition, English peppermint is grown in Kent, Suffolk, Hertfordshire, Cambridgeshire and Lincolnshire.

The plants are propagated by means of roots, and not by seeds.

## P E R F U M E R Y

After the land has been ploughed and manured during the winter, the plants are set in May. The best yield is obtained in the second year, and after about five years the land is not again cultivated for peppermint for several years. Only one crop is gathered annually, commencing at the end of August or early in September.

In many distilleries old-fashioned stills, heated by direct fire, are in use. These stills take charges up to a ton or even more of herb, and the distillation lasts from five to six hours, the greater part of the oil coming over in the first two hours. There are, however, to-day a number of modern steam stills designed on the latest scientific principles, which obviate the possibility of burning the herb and so imparting a disagreeable flavour to the oil. The yield of oil per acre varies considerably, according to the character of the plants used, the amount of sunlight they receive, the manuring and cultivation, and various other conditions. Generally, it may be said to fall between 10 and 20 lb. per acre.

The black mint is cultivated more than the white mint, as it usually yields a larger percentage of oil. The following figures may be taken to represent the analytical characters of genuine English peppermint oils:—

|                                     |                  |
|-------------------------------------|------------------|
| Specific gravity . . . . .          | 0.900-0.912      |
| Optical rotation . . . . .          | -- 23° to -- 33° |
| Refractive index . . . . .          | 1.4600 1.4640    |
| Esters as menthyl acetate . . . . . | 3-21 per cent.   |
| Total menthol . . . . .             | 50-68 „          |
| Menthone . . . . .                  | 8-12 „           |

These figures must not be taken as absolutely conclusive, as oils will be found occasionally which vary a little outside these limits.

Apart from menthol and menthone, English peppermint oil contains a mixture of terpenes, a sesquiterpene, and acetic and isovalerianic acid in the form of esters.

**American Peppermint Oil.**—The exact differences between the English and the American peppermint plants are still a matter of doubt, but at all events the latter are nearer in their botanical relationships to the English forms than the French plants are. According to Henkel (*U.S. Dept. of Agriculture, Bureau of Plant Industry, Bulletin No. 90, Part III., 1905*), there are three kinds of peppermint cultivated in the United States, *Mentha pirpeita*, and two varieties, *vulgaris* and *officinalis*. The plants grow freely in many of the eastern States, from the New England States to Minnesota, and south to Florida and Tennessee. The black mint

(var. *vulgaris*) is the hardiest of the three mints, and gives a better yield of essential oil than the other two. It is therefore cultivated on nearly all the peppermint farms. The oil from the white mint is of very fine odour, but as the plant is rather sensitive and the oil yield low, it is not much cultivated to-day. Various forms of stills are used for the distillation of the oil, many of them being huge wooden vats capable of taking a charge up to 3,000 lb. of the herb.

Up till recently many of the complaints of disagreeable taste and odour which were made in regard to some American peppermint oils were due to the fact that there existed considerable carelessness in the gathering of the mint, so that other plants were present and were not sorted out before distillation. The particular offenders in this respect were *Erigeron canadensis*, *Erechtithites micracifolia*, *Hedeoma pulegioides*, and various *Ambrosia* species.

The original home of the distillation of the oil was in Wayne county, in the north-western part of the State of New York. Thence it spread, and in 1835 the cultivation of peppermint was introduced into Michigan, first into St. Joseph county. To-day Michigan is the principal oil-producing State. The most exhaustive examination of the constituents of American peppermint oil is that of Power and Kleber (*Pharm. Rundsch. New York*, 1894, 12, 157). The oil was found to contain the following substances, most of which were isolated by the chemists mentioned:—

|                    |                         |
|--------------------|-------------------------|
| Acetic aldehyde.   | Isovalerianic aldehyde. |
| Acetic acid.       | Isovalerianic acid.     |
| $\alpha$ -Pinene.  | Phellandrene.           |
| Cineol.            | <i>l</i> -Limonene.     |
| Menthone.          | Menthol.                |
| Menthyl acetate.   | Menthyl isovalerianate. |
| Cadinene.          | Amyl alcohol.           |
| Dimethyl sulphide. |                         |

In addition to these well-characterised substances there are also present the menthyl ester of an acid of the formula  $C_8H_{12}O_{27}$ , and a lactone of the formula  $C_{10}H_{16}O_2$  melting at 23°.

American peppermint oil has the following characters:—

|                   |       |                 |
|-------------------|-------|-----------------|
| Specific gravity  | . . . | 0.899–0.915     |
| Optical rotation  | . . . | — 20° to — 35°  |
| Refractive index  | . . . | 1.4600–1.4635   |
| Total menthol     | . . . | 48–63 per cent. |
| Menthol as esters | . . . | 5–9 „           |
| Menthone          | . . . | 9–16 „          |

Occasionally a sample will be found of undoubted purity which

## PERFUMERY

has characters outside these limits. For example, the menthone has been known to rise to as high a figure as 25 per cent.

Most genuine samples of American peppermint oil are soluble in 3 to 5 volumes of 70 per cent. alcohol, but sometimes with opalescence.

The flavour value of American oil is much superior to that of Japanese oil, but does not, of course, compare with that of English peppermint oil.

The following interesting details in regard to American peppermint oil are due to A. M. Todd (*P. & E. O. R.*, 1914, 252).

More than 100 years ago the cultivation of peppermint was begun in Wayne county, New York State, and was confined to that region for the next twenty-five years, until it was introduced into Michigan. After another quarter of a century the production in the latter State equalled the output of Wayne county. Up to about thirty years ago growers of peppermint believed that the herb would only thrive on the uplands, but when experiments were made in Kalamazoo county in the south of Michigan, and just to the north of the Indiana boundary, it was found that the rich black soil formed by the decay of aquatic plants, which at some remote epoch grew in lakes that are now dry land, gave marvellous results. The State of Michigan is rich in possessing several areas of such fertile land, hence the success that has followed mint culture in that region during the last thirty years, and the growing inability of Wayne county to compete with it. One would not call the south of Michigan picturesque, but broad expanses of dead-flat land, verdant with the evidence of a prospering industry, have a charm all their own, and are more restful to the senses than the majestic but sterile mountain peak.

Farmers in that part of the country often drive their ploughs for nine miles without turning. The land is ploughed into furrows 3 feet apart, and into them are planted in a continuous row "runners" propagated from the previous year's planting, 1 to 3 feet in length, and about a quarter of an inch thick. Under favourable conditions a shoot will grow up every few inches, and as soon as the rows are discernible above ground, hoeing and weeding are maintained until the plant is in bloom, which happens during August and September. At this period, when the plants contain their maximum of essential oil, they are mown down and dried as far as may be without their becoming so brittle that the leaves are lost in handling. The partially dried herb is then loaded into a train of waggons and transported by a traction



engine to the distillery. A charge of two tons is hoisted by a crane into each of a series of wooden vats, closed down by a steam-tight cover, steam is blown in at the bottom of each, and the mixture of essence and steam condensed in the usual manner, the floating oil being drawn off, dried, bulked, and filled into storage tanks.

The yield of oil depending upon weather conditions and soil, varies greatly from year to year. In some rare cases, where the growth is abnormally stalky, with scanty leaf and bloom, as little as 1 lb. from 1,000 lb. may be the product. On the other hand, under rare and extremely favourable conditions as much as 10 lb. per 1,000 lb. has been obtained, but, calculating on an average of ten years, Mr. Todd is content with a yield of 3 to 4 lb. per 1,000 lb. of partially dried herb. Years ago, when methods of distillation were crude and empirical, many small growers drew the oil from the produce of their own little holdings; but with the march of progress the industry is rapidly getting into the hands of a few large houses who have capital to expend on greater and improved distilleries and costly experiments. The result, of course, is a more uniform, more copious, and an altogether better production of essence.

**Japanese Peppermint Oil.**—Japanese peppermint oil is in no sense a competitor with the English or American oils. It is derived from a different plant, has a bitter taste, and is only suitable for lower-grade work where delicate flavouring is not required.

There is a considerable difference of opinion as to the exact botanical relationships of the Japanese plant. The following details are given by the *Perfumery and Essential Oil Record* (1911, 7), and deal with both Japanese and Chinese peppermint :—

The Japanese peppermint, which is believed to have been cultivated for 2,000 years, is derived from a robust form of *Mentha arvensis*. In this species the flowers are arranged in a single ring in the axils of the upper leaves, which do not become smaller towards the top of the stem as in *Mentha sativa*. As illustrating the remarkable chemical difference that may occur in the same species of mint growing under different conditions, it may be pointed out that the form of *M. arvensis* growing in Ceylon has the odour of spearmint, and the form growing in Britain has quite a different odour, resembling that of horsemint; yet there are no botanical characters to separate these plants as species, except the more tapering teeth of the calyx in the Japanese plant, a feature which is common in Asiatic specimens of *M. arvensis*.

## PERFUMERY

The variety cultivated in Japan has been named *Piperascens*, and that cultivated in China, which has rather narrower and nearly glabrous or hairless leaves, has been named *Glabrata*. The plants of this species are not, like true peppermint, lovers of wet soil, but grow as weeds in sandy or light soil in open fields. The plant was experimented with in this country by Mr. John Moss in 1888 (*Pharm. Jour.*, 3, xix., p. 258), but in the conditions under which he cultivated it the plants grew 3 feet high, and were distilled before they were fully in blossom, and the yield of oil was only  $\frac{1}{2}$  per cent., somewhat less than half the yield obtained at Mitcham. It had a specific gravity of 0.9117 at 62° F. As compared with oil distilled from imported dried plants from Japan, the oil of the English-grown plants had a more powerful and penetrating, but softer odour. The oil did not deposit crystals of menthol, even when the bottle was placed in ice. Judging from the height of the plant, it appears to have been grown under conditions of moisture and shade quite foreign to the natural conditions of the species, which might account for the deficiency of menthol. Further experimental cultivation under more natural conditions is therefore desirable.

The Japanese peppermint is planted at the end of November and the beginning of December, and yields in the district of Kobe, in Bizen, Bitchu, and Bingo, three crops in the year, the first in July, the second in August and early in September, and the third at the end of September and the beginning of October. In Uzen, in the north-east, there are only two cuttings, which take place in August and September, and in Hokkaido only one, viz., in October and early November. The third crop yields most oil.

Briquet, the Swiss botanist, considers that the parent plant of Japanese peppermint is *Mentha canadensis* var. *piperascens*, which he regards as identical with the species E. M. Holmes describes as *Mentha arvensis* var. *piperascens*. This, however, is unlikely. Naojiro Irouge (*Schimmel's Report*, November, 1908, 199) has probably dealt with the question of Japanese peppermint oil more comprehensively than any other chemist. He considers that the present plant, of which four varieties are cultivated, is the product of numerous cultural improvements. He points out that Nagasaki (*Special Report on the Agricultural Experiment Station*, No. 4: "The Cultivation of Peppermint in Yamagata Prefecture," 1901) evidently accepts Holmes' identification, stating that Japanese peppermint is regarded as *Mentha arvensis*.

## P E R F U M E R Y

var. *piperascens* Holmes. Nagasaki describes the four cultural varieties as follows :—

(1) *Akamaru* (from *aka*, meaning red, and *maru*, round).—The leaves are round, the stem reddish-violet in colour, the flowers are faintly violet in colour. The content of the oil and menthol is much larger than in any of the other varieties.

(2) *Aomaru* (from *ao*, meaning green, and *maru*).—The leaves are round, the stem is blue, and the flowers faintly violet.

(3) *Akayanagi* (from *aka* and *yanagi*, willow).—The willow-like leaf is faintly violet on the lower surface, the stem is blue, the flower white. The percentage of oil is low.

(4) *Aoyanagi*.—The leaves are willow-like, the stem is blue, the flower white. It resembles the wild plant.

Of these four varieties, the first, or *Akamaru*, is regarded as the best, and is therefore most highly prized by cultivator, manufacturer, and merchant. However, it is impossible to plant only this variety at present (evidently because a sufficient number of plants cannot be obtained).

Japanese peppermint, when once planted, may be kept for harvesting for five to seven years, but it deteriorates in quality, and it is preferable to cut for three years only and then put in new plants, allowing a rotation of crops with, by preference, a leguminous plant. Propagation is effected by the cutting of runners, and not by seeds.

The oil is distilled in apparatus of a fairly primitive nature, and the essential oil, which contains the whole of the menthol, is known locally as *toriaroshi* by the Japanese. This oil is transferred to cans, which are placed in a freezing mixture, and a large portion of the menthol is thus crystallised oil. This, of course, is only practicable since Japanese peppermint oil contains far more menthol than any other peppermint oil. The separated menthol is exported as such, and the oil which drains off from the crystals forms the dementholised Japanese peppermint oil of commerce, which is the only oil which is sold on a commercial scale.

At ordinary temperatures natural Japanese peppermint oil is a crystalline mass saturated with oil. Such natural oil has the following characters :—

|                  |   |   |   |                    |
|------------------|---|---|---|--------------------|
| Specific gravity | . | . | . | 0.900–0.910 at 15° |
| Congeaing point  | . | . | . | 17°–28°            |
| Optical rotation | . | . | . | –28° to – 38°      |
| Total menthol    | . | . | . | 70–90 per cent.    |
| Menthyl acetate  | . | . | . | 3–8 „              |

## P E R F U M E R Y

The so-called dementholised oil has the following characters :—

|                            |                |
|----------------------------|----------------|
| Specific gravity . . . . . | 0.895–0.905    |
| Optical rotation . . . . . | – 26° to – 35° |
| Refractive index . . . . . | 1.4590–1.4630  |
| Menthyl acetate . . . . .  | 5–17 per cent. |
| Total menthol . . . . .    | 40–54 „        |

The following unpublished communication is due to Mr. M. Salamon (December 31st, 1924) :—

“Some recent deliveries of dementholised Japanese peppermint oil have been somewhat abnormal in odour, and on being subjected to fractional distillation have yielded a higher percentage than usual of low boiling fractions, and a lower percentage of the fraction distilling between 210° to 220°.

“This type of oil is characterised by having a comparatively low specific gravity, optical rotation, and refractive index, and the latter, in some of the samples examined, increased slightly after washing with warm water.

“It may be that these oils are adulterated with some foreign oil, but it appears more probable that they are dementholised peppermint oils that have been chemically treated in order to increase the yield of crystallisable menthol, and that in the process secondary reaction bodies have been formed which give rise to the peculiar odour that has been noticed.

“It is well known that some of the high molecular weight alcohols similar to menthol break down under certain treatment into alcohols of lower molecular weight, such as methyleyclohexanal, and a ketone, such as acetone, and the odour and certain of the chemical reactions of these oils suggest the presence of these bodies.

“The characters and fractionation of a sample of this type of oil were as follows :—

|   |                 |
|---|-----------------|
| Specific gravity at 15.5° . . . . .                     | 0.897           |
| Optical rotation . . . . .                              | 24.5°           |
| Refractive index at 25° . . . . .                       | 1.4597          |
| Refractive index at 25°, after washing . . . . .        | 1.4603          |
| Acetylisable contents (calculated as menthol) . . . . . | 52.5 per cent.  |
| Esters (calculated as menthyl acetate) . . . . .        | 6.75 „          |
| Solubility in 70 per cent. alcohol . . . . .            | 1 in 4 volumes. |

“On fractionation this oil yielded 12 per cent. distilling up to 200°, and only 26 per cent. distilling between 210° to 220°.

## P E R F U M E R Y

A normal dementholised oil does not usually yield more than about 6 per cent. distilling up to 200°, and yields at least 40 per cent. that distils between 210° to 220°."

We may now pass on to a short consideration of French, Italian, German, and Russian peppermint oils, which are to some extent commercial articles in this country.

**French Peppermint Oil.**—In France peppermint is cultivated in the department Alpes-Maritimes, in the vicinity of Grasse, Cannes, Vence, Cagnes, and Villeneuve-Loubet; in the department Basses-Alpes, near Entrevaux, Barremer, and Castellana; in Var, near Fayence; in Haute-Garonne, near Revel; and in Vaucluse. The question of the plants cultivated in France has been dealt with in describing the English peppermint plant. The so-called *Menthe basiliquée* is a degenerated peppermint plant which has been attacked by an animal parasite, the *Eryophyes Menthae*. The oil yielded by such plants is of a very inferior quality. French peppermint oil has the following characters:—

|                            |               |
|----------------------------|---------------|
| Specific gravity . . . . . | 0.910–0.927   |
| Optical rotation . . . . . | – 5° – 35°    |
| Refractive index . . . . . | 1.4620–1.4715 |
| Total menthol . . . . .    | 4–20 per cent |
| Combined menthol. . . . .  | 45–70 ..      |

Many French oils are not completely soluble in 3 to 4 volumes of 70 per cent. alcohol.

The oil from the diseased plants above referred to frequently has a dextrorotation up to + 7°, and the total menthol frequently falls to 40 per cent.

*Roure-Bertrand Fils* (*Bulletin*, April, 1909, 33) have drawn attention to the fact that oil of peppermint distilled at Grasse does not crystallise even when cooled to – 17° C. and sown with crystals of menthol. In an exhaustive examination of the oil they established the presence of the following compounds: valerianic aldehyde, iso-amyl-alcohol, *l*-pinene, *p*-menthene, cineol, *lævo*-menthol melting at 42°, and *dextro*-menthone.

Dr. Ripert, the Director of the Franco-Mitcham Co-operative Agricultural Society, gives the following analyses (*Pamphlet* No. 17) of oils distilled from black mint plants originating from Mitcham and cultivated in various parts of France.

**Italian Peppermint Oil.**—Much of the peppermint cultivated in Italy is of indefinite origin, but plants derived from English stock are also being cultivated at Pancalieri in Piedmont.

# PERFUMERY

| Place of growth and year.  | Yield<br>per<br>1,000. | Esters,<br>p.c. | Menthol<br>total,<br>p.c. | Menthol<br>free,<br>p.c. | Menthol<br>esteri-<br>fied,<br>p.c. | Menth-<br>one,<br>p.c. | Solu-<br>bility in<br>alcohol<br>70° C. | Rotatory<br>power at<br>20°. | Refractive<br>index at<br>8°. |
|--|------------------------|-----------------|---------------------------|--------------------------|-------------------------------------|------------------------|---|------------------------------|-------------------------------|
| Dol in Brittany, 1922 . . .  | 1.9                    | 4.82            | 51.51                     | 47.51                    | 3.68                                | 22.42                  | 3.2                                     | — 26°                        | 1.4631                        |
| Chartres (Rennes), 1922 . . .  | 2.3                    | 11.43           | 50.84                     | 40.35                    | 8.84                                | 24.58                  | 3.4                                     | — 25°                        | 1.4659                        |
| Garden of the Laboratory of<br>Agricultural Botany of the<br>Rennes Faculty of Sciences,<br>1922 . . . | 2.5                    | 4.62            | 44.22                     | 40.22                    | 3.64                                | 21.32                  | 4.12                                    | — 27°                        | 1.4657                        |
| Chartres (two-year-old plant),<br>1923 . . .   | 0.95                   | 3.96            | 49.90                     | 47.51                    | 3.14                                | 18.37                  | 3.6                                     | — 23°                        | 1.4652                        |
| Garden of the Laboratory (two<br>years), 1923 . . .  | 1.45                   | 6.90            | 54.91                     | 47.90                    | 5.37                                | —                      | 3.5                                     | — 24°                        | 1.4660                        |
| Dinan (Brittany) . . .   | 3                      | 4.90            | 50.84                     | 45.53                    | 3.86                                | —                      | 3.2                                     | — 22°                        | 1.4645                        |
| St. Sulpice sur Leze (Hte. Garonne),<br>1923 . . .   | 5.32                   | 4.66            | 50.77                     | 46.32                    | 3.70                                | 18.23                  | 3.3                                     | — 21°                        | 1.4652                        |
| Oise, 1923 . . .   | 5.50                   | 5.94            | 56.60                     | 49.50                    | 4.68                                | —                      | 3.5                                     | —                            | 1.4659                        |
| Mint from Nice, grown at Rennes<br>--pseudo-Mitcham . . .  | 4.37                   | 13.20           | 48.83                     | 35.92                    | 10.40                               | 12.62                  | 3.4                                     | — 16°                        | 1.4670                        |

The Italian oil has a flavour and an odour which depend on the source of the plants distilled. The characters are as follows :—

|                            |                 |
|----------------------------|-----------------|
| Specific gravity . . . . . | 0.909–0.925     |
| Optical rotation . . . . . | —5° to —27°     |
| Refractive index . . . . . | 1.4620–1.4680   |
| Total menthol . . . . .    | 45–65 per cent. |
| Combined menthol . . . . . | 3–10 „          |

The oil is usually soluble in 3 to 7 volumes of 70 per cent. alcohol.

**German Peppermint Oil.**—A small amount of peppermint oil of excellent odour is produced in Saxony, the price being very high and the oil greatly esteemed. It has the following characters :—

|                            |                    |
|----------------------------|--------------------|
| Specific gravity . . . . . | 0.900–0.915        |
| Optical rotation . . . . . | —23° to —37°       |
| Refractive index . . . . . | 1.4580–1.4690      |
| Acid value . . . . .       | 0–1.3              |
| Combined menthol . . . . . | 2.8–20.8 per cent. |
| Total menthol . . . . .    | 48–81 „            |
| Menthone . . . . .         | 12–23 „            |

Thoms (*Apoth. Zeit.*, 28, 672) has published a note on the production of menthol in Germany and its (late) south-west African colonies. He describes the essential oils distilled from plants of Japanese origin, obtained at Dahlem (first and second cutting), at the colonial college at Witzenhausen, and at Okahandja (Africa). The results of the analyses of the chief of these oils are summarised in the following table :—

|   | Dahlem.<br>(First cutting.) | Witzenhausen.   | Okahandja.<br>(Leaves.) |
|---|-----------------------------|-----------------|-------------------------|
| Specific gravity . . . . .              | 0.8987 at 18°               | 0.9012 at 15.5° | 0.9012 at 20°           |
| Solidifying point . . . . .             | + 13.5°                     | + 14.5°         | + 20.75°                |
| Optical rotation at 20° . . . . .       | — 35.55°                    | — 35.29°        | — 35.29°                |
| Acid value . . . . .                    | 2.66                        | 3.32            | 1.56                    |
| Ester value . . . . .                   | 12.96                       | 15.15           | 8.29                    |
| Ester value after acetylation . . . . . | 283.82                      | 291.61          | 306.56                  |
| Combined menthol . . . . .              | 3.78 per cent.              | 6.99 per cent.  | 2.31 per cent.          |
| Free menthol . . . . .                  | 75.20 „                     | 74.16 „         | 83.01 „                 |
| Total menthol . . . . .                 | 78.98 „                     | 81.15 „         | 85.32 „                 |

**Russian Peppermint Oil.**—A small quantity of Russian

## P E R F U M E R Y

peppermint oil is produced annually, but not sufficient to influence the peppermint oil market. The description of Russian peppermint oil here given applies equally to the oil produced in those independent territories which were until a few years ago a portion of Russia itself. The mint used for distillation appears to be a variety of *Mentha piperita*, similar to, if not identical with, that cultivated in England (black mint). From 1.6 to 1.7 per cent. of oil is obtained from the plants. The oil has the following characters :—

|                          |                |
|--------------------------|----------------|
| Specific gravity . . . . | 0.900–0.920    |
| Optical rotation . . . . | — 17° to — 28° |
| Refractive index . . . . | 1.4584–1.4707  |
| Combined menthol . . . . | 3–21 per cent. |
| Total menthol . . . .    | 40–60 „        |

Maisit (*Arch. du Pharm.*, 1911, **249**, 637) has published an interesting account of the Russian peppermint industry, to which reference should be made for further information.

Nakao and Shibuye (*Yakugakuzasshi*, September, 1923; and *Chemist and Druggist*, December, 1923, 898) have made an interesting observation in regard to Manchurian peppermint oil. They find that the menthol content of peppermint oil distilled from mint grown in Manchuria decreased year by year, and after a few years the oil no longer yields any crystals of menthol. For this reason the cultivation of peppermint in Manchuria, which at one time appeared so promising, has now been considerably curtailed. An examination of a specimen of degenerated oil showed it to possess the following constants: specific gravity at 15°, 0.916; acid number, 0.535; ester value, 139.96; ester value after acetylation, 235.48; optical rotation, — 54.59°. The authors assumed that the menthol contained in the oil is present in the form of esters, and on saponifying the oil they succeeded in obtaining almost the theoretical amounts of menthol and of acetic acid, and a small amount of valerianic acid. In addition, they were able to demonstrate the presence of menthone and limonene.

For other peppermint oils, which are of little or no commercial importance, references as follows may be made :—

DALMATIAN OIL : *Schimmel's Bericht*, 1911, October, 69.

HUNGARIAN OIL : Irk, *Kísérletügyi Közleményik*, 1910, **13**, 3; and E. J. Parry, "The Chemistry of Essential Oils," 4th ed., vol. i., p. 234.

BOHEMIAN OIL : *Schimmel's Bericht*, 1896, April, 47

JAVAN OIL : *Roure-Bertrand Fils, Bulletin*, 1910, **3**; **1**, 59.



BRITISH EAST AFRICAN OIL : *P. & E. O. R.*, 1915, 4.  
 CHINESE OIL : *Daily Cons. and Trade Report* (Washington),  
 1914, 17 ; 56, 906.

WEST AUSTRALIAN OIL : E. J. Parry, *P. & E. O. R.*, 1924, 188.

**PERFUME IN THE PLANT.**—The genesis and functions of perfumes in plants are subjects of intense interest, and upon them much speculation has been spent. And although this branch of physiological botany is still but little understood, its relations with the chemistry of the perfume material, and consequently with the commercial aspect of the manufacture of raw materials for perfumery, are steadily being developed.

Whilst it may be true that the essential oils which constitute the perfume material of plants are, so to speak, by-products of the metabolic processes of cell life, and as such to be classed with alkaloids, tannins, and colouring matters, it is impossible to overlook the enormous importance of the perfume in the plant economy in attracting insects for the purpose of fertilising the flower. It is, of course, true that some flowers are odourless whilst the green leaves are highly odorous—as in the geranium ; and also that the essential oil is frequently to be found in almost all parts of the plant, including the root. But in the former case the insect will be attracted by the 'perfume of the leaf, and so brought within range of the coloured flower which he will then visit ; and in the latter case, it may frequently be that the oil is being manufactured by steps in the plant, and its presence in parts of the plant remote from the flower merely indicates one of the steps of its evolution, since the oils from different parts of the same plant are usually different in character.

Whether or not this is the principal physiological function of the perfume in the plant can scarcely be said to be known, but there are many remarkable correlations between flower perfume and animal life. One of these is the development of the perfume simultaneously with the time of flying of certain insects. The flowers of certain species of honeysuckle, those of certain petunias, and those of *Hyabenaria bifolia*, and many other plants are visited to a considerable extent by crepuscular lepidoptera. These plants smell faintly or not at all during the daytime. But after sunset, from about six to seven in the evening until midnight, they give off an abundant odour. The flowers of *Hesperis tristis*, and numbers of the caryophyllaceous plants, which are visited by small nocturnal moths, give off no perfume during the day, but exhale a powerful hyacinth-like odour at night. The same is

true of many other flowers. It is equally true that many flowers which are regularly visited during the daytime by bees and butterflies are odorous during the day, but nearly odourless at night. The yellow flowers of *Spartium scoparium* only give off their exquisite cassie-like perfume when the sun is high and the insects named are flying about. In the evening the perfume practically disappears. The flowers of *Trifolium resupinatum* have a powerful honey odour in the sunshine when the bees are about, but become odourless, or nearly so, at twilight, by which time the bees are back in their hives. Tyndall suggested that the essential oils, especially when the secretion takes place near the surface of an organ, may have a function in the regulation of the rate of transpiration. Solutions of essential oils in water, or emulsions of the two bodies, not only have heat conductivities different from that of water itself, but also considerably affect the osmotic pressure, so that circulation and transpiration may be affected considerably by the essential oils. It has also been suggested that the high rate of consumption of essential oil during the fecundation period points to easy assimilation and a high nutritive value of its constituents.

The actual mechanism by which the essential oil is built up or synthesised in the plant is practically unknown. It is, however, noteworthy that, with very few exceptions, all the perfume bodies which are in the plant built up at a low temperature require elevated temperatures for their artificial production, where this is possible, in the laboratory. What the vital principles are that render this "cold" synthesis possible are quite unknown. A view which has quite recently been put forward by Francesconi, Manfredi, and Astengo, in a paper read before the First Italian Congress on Pure and Applied Chemistry, held in Rome in 1923, is that isovalerianic aldehyde,  $\text{CH}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{CHO}$ , is the fundamental substance from which the plant derives its terpene and sesquiterpene compounds. This aldehyde was found in the essential oils of lemon, orange, bergamot, and tangerine. It was suggested that the origin of this body is isoamyl alcohol, formed by the fermentation of albuminoids or carbohydrates, or both.

Such a view would involve the assumption that the very complex bodies, the carbohydrates and albuminoids, were first built up, then broken down to a still fairly complex aldehyde, from which the essential oil is then built up.

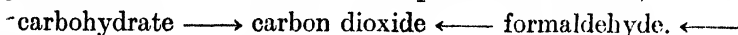
It is, of course, an established fact that the green parts of plants, which contain chlorophyll, the leaves particularly, absorb

carbon dioxide from the air in the presence of sunlight and evolve oxygen in equimolecular proportions. So long ago as 1870 B  yer (*Berichte*, 1870, 3, 67) suggested that formaldehyde was the primary product of the carbon dioxide assimilation, and that carbon dioxide and water each lost an atom of oxygen, and the residues = CO and H<sub>2</sub> combined to form CH<sub>2</sub>O, formaldehyde.

Simpson (*P. & E. O. R.*, 1923, 113) summarises a good deal of recent work which has been done in this direction :—

Processes resembling the reactions which may occur in plants have been carried out quite recently by Baly and Heilbron (*Jour. Chem. Soc.*, 1921, 119, 1025 ; 1922, 121, 1078), who have obtained formaldehyde from carbon dioxide by the action of light of definite wavelengths. Carbon dioxide absorbs ultra-violet light of wavelength 200  $\mu\mu$ , and formaldehyde that of wavelength 290  $\mu\mu$ . Baly and Heilbron showed that, if carbon dioxide is bubbled through a saturated aqueous solution of carbon dioxide exposed to ultra-violet light of the shorter wavelength, but protected, by the addition of an inert substance, from light of the longer wavelength, then formaldehyde is produced and accumulates. Such inert protective substances are paraldehyde, sodium phenoxide, and the inorganic salts, ferric chloride and uranium nitrate, which Moore and Webster (*Proc. Roy. Soc.*, 1914, B, 87, 163, 556) had supposed to act as chemical catalysts for the conversion of carbon dioxide into formaldehyde under the influence of ultra-violet light. When, however, the aqueous solution of carbon dioxide was not so protected, or when a solution of formaldehyde was exposed to ultra-violet light of wavelength 290  $\mu\mu$ , the formaldehyde was polymerised and reducing sugars were obtained.

The fact that Moore and Webster (*loc. cit.*) found that chlorophyll, carbohydrates, and other substances of biochemical origin yielded formaldehyde on exposure to ultra-violet light does not, as they supposed, disprove the formation of formaldehyde as an intermediate between carbon dioxide and carbohydrates, for when acetone is photochemically decomposed, not formaldehyde, but carbon dioxide, is formed. Hence Baly and Heilbron assume that the formaldehyde produced by the decomposition of carbohydrates must be the result of an equilibrium reaction, such as



Moreover, when an aqueous solution of acetone is exposed to the ultra-violet light of a quartz lamp, reducing sugars are produced, and these must have been synthesised from the carbon dioxide *via* formaldehyde.

So far, however, the conditions which hold in the leaf of the plant have been disregarded, for in ordinary daylight there is very little light of wavelength as short as  $200\ \mu\mu$ . Further, plants grow perfectly normally in light transmitted through glass which completely absorbs light of wavelengths less than  $350\ \mu\mu$ , although outside the plant no formaldehyde is formed from carbon dioxide and water under the influence of light with greater wavelengths than  $350\ \mu\mu$ .

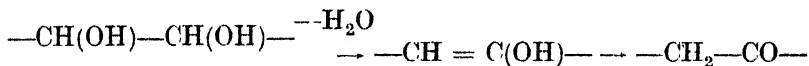
This, however, does not mean that the reaction cannot take place under the influence of light of wavelength greater than  $350\ \mu\mu$ , for Baly and Heilbron (*Jour. Chem. Soc.*, 1921, 119, 653) have shown that energy may be transmitted from one molecule to another when these possess a common absorption frequency in the infra-red portion of the spectrum. Hence, if in the leaf there is a substance which absorbs the infra-red rays having a frequency identical with those absorbed by carbon dioxide, but which also absorbs visible light of a characteristic frequency, then the energy of the visible light so absorbed may be radiated by this molecule in the form of infra-red rays and reabsorbed in this new form by the carbon dioxide. Such substances are termed photocatalysts.

In the plant there are undoubtedly photocatalysts present which absorb visible light and radiate it as infra-light of frequencies absorbed by the carbon dioxide and formaldehyde respectively, causing (1) the conversion of carbon dioxide into formaldehyde, and (2) the polymerisation of formaldehyde into reducing sugars. Photocatalysts which allow the first reaction to take place, but protecting, at least in part, the formaldehyde formed from polymerisation, are malachite green, *p*-nitrosodimethylaniline, colloidal uranium, and colloidal ferric hydroxide. In the plant itself the chlorophyll undoubtedly acts as a dual photocatalyst for the two reactions. The function of the chlorophyll was concisely and prophetically summarised by Mrs. Helen Abbott Michael in a lecture delivered before the Franklin Institute in January, 1887, as follows: "It absorbs certain rays of light, and thus enables the protoplasm of the cell to avail itself of the radiant energy of the sun's rays for the construction of organic substances from carbon dioxide and water."

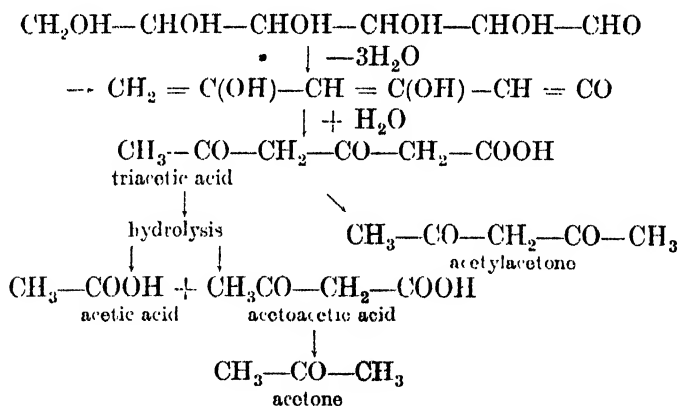
Such energy as is absorbed in the form of light by the organs of the growing plant is stored, in its converted form, as chemical energy, especially in the form of starch, insulin, and proteins; and, as Simpson points out (*loc. cit.*), the first step in the utilisation of

## P E R F U M E R Y

the chemical energy of the starch is its hydrolysis, by enzymes, to maltose, and thence to glucose, in which form, in solution in the sap, it can be transferred to any required part of the plant. The next stage, the degradation of the simpler carbohydrates, seems to be the formation of substances containing the keto-methylene grouping,  $-\text{CH}_2\text{CO}-$ , or chains of this grouping, which may be considered as being derived from carbohydrates by a single dehydration and the migration of a hydrogen atom, thus :—



The importance to plant physiology of the readiness with which substances containing this ketone grouping condense with one another and with other substances was first recognised by Collie (*Jour. Chem. Soc.*, 1907, **91**, 1806), and if we apply the above series of changes to a simple aldohexose sugar, the product will readily furnish us with a number of substances from which a good many essential oils are very probably synthesised by the plant, thus :—



From acetic acid there may also be formed, by reduction, acetaldehyde and ethyl alcohol, and methyl alcohol may likewise be formed from formaldehyde.

The identification, however, of any of these or other simple substances, for example methyl alcohol, ethyl alcohol, acetaldehyde, diacetyl, or methyl heptenone, in the lower fractions of the essential oils, neither proves nor disproves that these bodies are the precursors of the more important constituents, since they may be equally readily produced from the terpenes by breakdowns

## PERFUMERY

occurring during the preparation of the oil, particularly by fermentation or during distillation.

Charabot, who has made an exhaustive study of the development of the perfume in the plant, gives the following *résumé* in a highly interesting brochure, "The Present State of the Perfume Industry" (Paris, 1909):—

"The study of the mechanisms which regulate the formation of the odorous matters, and their evolution, the investigation of the relations existing between the chemical phenomena which modify these substances and the immediate manifestations of the life of the plant, the knowledge of the part played by the essential oils in the vital economy, constitute so many enticing problems which, it will be readily conceived, have a capital importance, not only from the point of view of rational cultivation and of judicious harvesting, but also from the point of view of the rational extraction of the perfume of the plant.

"To this study I have devoted, either alone or in collaboration, principally with M. Al. Hébert, more than ten years of research work.

"The question embraces: the formation and circulation of the odorous compounds; their evolution, and the mechanism of this evolution; the genesis of the odorous matters, and the physiological rôle of the perfumes.

"*Formation and Circulation of the Odorous Compounds.*—The odoriferous plants form two very distinct groups as regards the distribution of their aromatic principles among the various organs. In some the essential oil makes its appearance in the green organs; in the others it exists exclusively in the flowers. Thus it will be necessary to consider separately the perfume in the entire plant and the perfume in the isolated flower.

"*The perfume in the entire plant.*—We have experimented with various representatives of the vegetable kingdom, belonging to different families and containing the most diversified chemical substances, and we have arrived at the following conclusions:

"The odorous matters make their appearance in the young green organs. They continue to form and accumulate until the flowering period, but with an activity which slackens more or less appreciably. They migrate from the leaf into the stem, and thence into the inflorescence, obeying the laws of diffusion; a portion enters into solution and, by osmosis, penetrates into the stem. On arriving in a medium already saturated with similar products, a portion is precipitated, whilst the rest, consisting of a

relatively soluble mixture, continues to diffuse through the membranes and reaches the organs of consumption, particularly the inflorescences.

"At the time when the work of fertilisation is accomplished, a certain quantity of essential oil is consumed in the inflorescence. It is possible, and even probable, that the green organs produce at the same time further quantities of odorous matters; experiment only permits of the determination of the fact that the difference between the production and consumption is expressed by a loss at the period when the functions of the flower are accomplished.

"The practical consequence of this last conclusion is that the harvesting of the perfume-yielding plants should be effected shortly before this consumption takes place, that is, before the act of fertilisation.

"When this act has been accomplished, the odorous principles appear to descend again into the stem and, generally, into the organs other than the flower, a migration which is probably induced by the desiccation of the inflorescences, which involves, other things being equal, an increase in the osmotic pressure and a partial precipitation *in situ* of the least soluble principles.

"*The perfume in the isolated flower.*—There exist, as was supposed by J. Passy, and as was proved by A. Hesse and his collaborators, two categories of plants: one class continuing to produce odorous matters when placed under conditions such that the vital functions may still be exercised; the other class containing the whole of their odorous principles in the free state, and incapable henceforth of producing any further quantity even though their vitality be not arrested.

"*Evolution of the Odorous Compounds, and its Mechanism.*—These researches, which I have carried out partly in collaboration with M. A. Hébert, have led to the following conclusions: The compound ethers have their origin, in particularly active fashion, in the green portions of the plants, by the direct action of the acids on the alcohols previously formed. This phenomenon of esterification is assisted by a special agent playing the part of a dehydrating agent, probably an enzyme of reversible activity.

"The influences which are capable of modifying the plants so as to adapt them for a more intense chlorophyllian function are favourable at the same time to esterification, because this function is favourable to the mechanical elimination of water.

"Thus the chlorophyllian function tends to acquire a new sig-

nificance : it not only assures the fixation by the plant tissues of carbonic acid gas, it not only effects, by favouring transpiration, the circulation of the liquids which carry and distribute the principles necessary to the mineral nutrition of the plant, but it also activifies, once the carbon is assimilated, the condensations which enable the passage from a simple chemical structure to one of the innumerable complex structures the study of which taxes all the ingenuity of the chemists.

“ When the alcohol is capable of readily parting with the elements of water, it gives rise, together with the compound ethers, to the corresponding hydrocarbon, so that the first transformations which the alcohols undergo are due to phenomena of dehydration.

“ Phenomena of isomerisation, that is, changes of nature without change of composition, also proceed together with the metamorphosis of the odorous matter. Lastly, the alcohols and their ethers are actively converted into their oxidation derivatives, particularly when the inflorescences appear, in which organs the fixation of oxygen by the tissues is particularly intense.

“ *Genesis of the Odorous Matters.*—The sum of my researches and the interesting observations of M. Hesse lead to a conception of the genesis of the odorous matters in the plant. A large number of the odorous products, very diverse in their functions and chemical structure, are produced in consequence of the splitting up, with fixation of the elements of water, of principles called glucosides. It is sufficient to admit the general nature of such a mechanism to arrive at a satisfactory explanation of the facts observed with regard to the formation of the odorous matters and their appearance at any particular point of the vegetable organism.

“ It seems to me that there is reason to believe that the glucoside which is capable of yielding the essential oil is formed or tends to be formed in the green portions. Most frequently, this glucoside immediately encounters the conditions of environment which are favourable to its decomposition, and then the essential oil appears in the green portions and begins to circulate, evolve itself and play its part. It may even happen that the medium is so favourable to the splitting up of the glucoside, that the latter can never be formed ; in this case the whole of the essential oil will exist in the free state in the green organs.

“ In other cases, the glucoside only comes in contact with the ferment which is capable of splitting it, in the flower. It will then



only be after it has circulated as far as the flower, undergoing in its course more or less profound modifications, that it will be able to liberate the constituents of the essential oil, and the flower alone will be odorous. It is not impossible that, in certain flowers, the medium may be so favourable to the splitting up of the glucoside, that the latter is completely split up as soon as it arrives there. The formation of further quantities of essential oil in certain flowers in proportion as the essential oil already formed is removed, would be explained by a phenomenon of chemical equilibrium. The following reaction: 'Glucoside + water = glucose + essential oil,' would be restricted by the reverse reaction, and a state of equilibrium would be reached when the glucose and the essential oil would amount to a certain proportion. Thus the flowers in question, if left to themselves, would retain a quantity of perfume which would not increase. On the other hand, if the essential oil be removed as fast as it is formed, the decomposition of the glucoside would no longer be limited, but would continue to take place. Consequently, the appearance of a fresh quantity of perfume in the plant whose life is prolonged whilst the odorous matter is continuously removed, follows as the result of a phenomenon of chemical equilibrium in the vegetable cell.

"It will be understood, without it being necessary to insist on it, what advantage we have been able to derive from the practical standpoint as regards the value and the yield of perfume, from all these results obtained by scientific research.

*Physiological Rôle of the Odorous Matters.*—In collaboration with M. Hébert, I have proved that, contrary to what was previously believed, the odorous matters are not waste products of which the plant cannot make use. They are capable of being utilised by the plant, particularly when the latter is protected from light and no longer assimilates the carbonic acid of the air with the same intensity. They participate normally in the work of fertilisation and of the formation of the seeds, in the course of which they are partially consumed.

"It might appear that the method of volatile solvents, with recent improvements, would have satisfied all possible desiderata. But progress is indefinite; its limits recede as fast as research tends to attain them. And there is no scientific or industrial problem which, when solved, does not open up a new problem. For instance, as a corollary to the researches of which I have just summarised the results, the question arose whether Nature has

not been too parsimonious in the distribution of her perfumes. In other words, there was reason to inquire whether it were not possible to modify the processes of the living cell in such a manner as to favour the elaboration of the perfume. This idea may appear to be a little Utopian, but if the idea is propagated, may it not be true that the Utopia which it discovers to-day will be the reality which progress will vanquish to-morrow? I have good reasons for saying that this is indeed a fact in the present instance. It will be seen therefore, that by enlarging the domain of vegetable chemistry and physiology, the study of the odorous matters has not merely been of speculative interest, but has also led to industrial applications in the most directly positive sense."

The essential oils are in most cases normal secretions, but a few are purely pathological products, their existence being brought about only by intentional wounding of the plant tissues. But, as animal secretions are often influenced by external conditions, so are plant secretions rendered abnormal by exposure of the plant to unusual conditions. Sometimes these alterations may be, from our point of view, beneficial, or they may be detrimental. The external conditions which have most influence on the life history of the plant in relation to its essential oil production are dependent upon (1) soil, (2) light, (3) moisture, (4) disease induced by insects. In regard to the soil, it is easy to understand that the whole life history of a plant must be largely influenced by the proper or improper supply of such food as is absorbed by the roots, and, as will be shown in the sequel, the suitable application of manures to the soil is absolutely essential if the most profitable results are to be obtained. Suitable applications of the necessary ingredients to the soil have a definite influence on the plant structures, and these will vary the character of the essential oil secreted, qualitatively and quantitatively, under these external influences. For example, Charabot and Hébert have shown that where peppermint has been grown in a single field, suitable additions to the soil have caused the oil to become dextrorotatory, whereas in that part of the field where no such addition has been made the plants yield a levorotatory oil. So also was the amount of esters increased by the addition of suitable mineral salts, and the percentage of menthone sensibly reduced.

Light, of course, has more influence on plant life than any other external influence. It would therefore be almost axiomatic that variations in this factor would cause variations in the character of the essential oil produced by the plant. Increased intensity of

illumination enlarges, *inter alia*, the size of the secreting vessels, and stimulates the activity of the chlorophyll. A material alteration in the ratio of oxygenated to terpene compounds in the essential oil is brought about by drastic changes in illumination.

The moisture in the atmosphere and soil has a very marked effect on the characters of the essential oil. For example, lavender plants which are grown in the Alps or in Dauphiné contain, as a rule, from 35 to 45 per cent. of linalyl acetate. But the same plants cultivated in the neighbourhood of Paris, with far more moisture in the atmosphere and soil, have been found to yield an oil containing only 10 per cent. of this ester. It is often said that the altitude at which plants are grown is an important factor in the determination of the characters of the essential oil. This, however, must be accepted with the following qualification. Temperature, moisture, and illumination may, and usually do, vary considerably with variations in altitude. It is the sum of the variations in these three conditions which really constitutes the variation due to altitude. In the same way, the so-called influence of locality as distinguished from altitude is really the sum of the influences of soil and climate. These may, of course, be so great as to cause the resulting essential oils to vary enormously according to their place of origin. For example, the oil distilled from *Cymbopogon Martini* in India contains about 90 per cent. of the alcohol geraniol, whereas the oil distilled from the same plant growing in New Caledonia contains only about 10 per cent. of this constituent. Numerous examples of similar variations exist, and, as a rule, where such differences exist the compounds existing in the two oils, although quite different, have usually a close chemical relationship. For example, the cymbopogon oil of New Caledonia contains over 40 per cent. of citral, which is the aldehyde corresponding to geraniol.

The influence of parasitic diseases on the essential oil is well illustrated by the case of what the French term *menthe basiliquée*. In the environs of Grasse peppermint plants are often found to be attacked by an insect, *Eriophyes Menthae*, one of the *Phytopyides*, which completely transforms the appearance of the plants, so that they closely resemble the tops of the sweet basil, *Ocimum Basilicum*; hence the name *menthe basiliquée*. No flowers are developed, and the essential oil distilled from such plants is of an entirely different character from that of normal peppermint oil. It contains a much higher percentage of esterified menthol, but only traces of menthone. Menthyl valerianate is present in the normal

oil to a greater extent than in the oil from the diseased plant, and the oil is frequently dextrorotatory, whereas the normal oil is lævorotatory. It is strange that the tendency of the free alcohol present to esterification exists where there is excessive dryness or much sunshine at the place of growth of the plant, and is also induced by pathological conditions such as that indicated above.

Those organs which contain the essential oil are termed the secreting organs. They are described concisely by Eugene Charabot ("Le Parfum chez la Plante," p. 167 *et seq.*). Many plant organs contain cells in which the essential oil is found. These cells exist in many parts of the plant, frequently in the parenchyma and epidermis of the petals of the flower, or in the epidermis of the scales enclosing young buds. Sometimes these secreting cells take on a specialised form and form secreting hairs or glandular hairs. These exist in very varied forms, but are always produced from the epidermis. They may consist of a single elongated cell or of a number of elongated cells placed end to end, or sometimes in the form of several layers of superimposed cells. Sometimes the terminal cell is sharply pointed; frequently it is globular and divides, by the formation of membranes, into several cells. Hanstein, and Tschirch and Tannmann consider that the essential oil is formed at the expense of the cell membranes, which undergo a sort of gelatinisation and break down into a mixture of mucilaginous matter and essential oil. This view is not shared by numerous other investigators, however, and cannot be said to be established.

The secretions known as "external" are produced in a cavity surrounded by living cells, which are known as secreting cells. This cavity may be spherical or in the form of a "canal," or in some intermediate form. They are usually classified according to their origin, which may be *schizogenous* or *lysigenous*, or intermediate between the two.

In such plants as for example the *Myrtaceæ*, the secretory pockets or canals are formed by the schizogenous process. A single cell divides into four daughter cells by the appearance of appropriate septa, which leave a space between the newly formed cells. The process is repeated again and again, the lacuna so formed continually increasing in size, which is the schizogenous gland. If this process takes place with numerous layers of cells, a canal is formed instead of only a gland or "pocket." The essential oil is formed in the living secreting cells bordering on

the gland or canal, and transfuses ready made into the gland or canal through the cell walls. In freshly formed organs of this type the essential oil sometimes appears first in the gland, etc., and only afterwards in the secreting cells. This is explained by Tschirch as being due to the decomposition of cell membrane as the mother substance of the essential oil. According to him the external part of the membranes of the cells immediately surrounding the organs rapidly becomes mucilaginous and oily, and the products so formed are the first which are present in the organ. This process continues until the gland or canal is completely surrounded by this gelatinous external layer of the surrounding cells, which Tschirch calls the resinogenous layer (*resinogeneschicht*). This layer, he considers, is separated from the canal or gland by a thin cuticle common to all the cells. In this resinogenous layer Tschirch considers the essential oil is formed, and transfuses into the gland or canal, where it agglomerates into drops. This, however, is still a matter of speculation. If essential oils and resins were completely insoluble in water, Tschirch's theory of the formation of the essential oil *outside* the surrounding cells would be understandable, as they could not then diffuse through the cell walls. But as these bodies are, in fact, soluble in water to a limited extent, there is nothing to stop them diffusing through the cell walls in the form of an aqueous solution, and the resinogenous layer, whilst possible, is no longer a necessary conception. Glands and canals of lysigenous origin are formed as follows :—

In a number of plants the “ external ” secreting organs are not formed by the splitting of cells with a shrinkage from each other, but by an actual dissolution of the cells themselves. In this actual dissolution of the cells there is, according to Tschirch, still the formation of a resinogenous layer, which functions as above indicated. These lysigenous spaces formed by disintegration of whole cells are not common in the vegetable world, and are usually the result of pathological conditions. And even where the cavities are lysigenous in origin the greater part of the cavity is formed by the schizogenous method, the final layer of cells bounding the space then disintegrating. The resin ducts of the *Conifers* are of purely lysigenous origin, but those of the *Rutaceæ* and many other plants have a mixed origin, which is termed schizolysigenous.

Secretory glands known as intercellular glands are found in one or two natural orders. These are spaces which appear between the secreting cells, which remain attached at their extremities, but are forced apart by the transfused secretion through the walls

of the cells to provide space for the accommodation of the secreted material.

The actual course of the evolution of the perfume in the plant has been followed in detail by Charabot and Laloue in a number of entirely different types of odour-bearing plants, of which the following are the principal : (1) the linalol group, (2) the geraniol group, (3) the thujol group, and (4) the menthol group. (*Vide Roure-Bertrand Fils, Bulletin, March, 1900, 12.*) The perfume of bergamot oil is almost entirely due to the acetic ester of the alcohol linalol. By dehydration linalol is converted into terpenes (principally limonene), and by esterification into linalyl acetate. They showed that as the bergamot fruit matures the following modifications happen to the essential oil :—

- (1) The amount of the free acids present decreases.
- (2) The amount of linalyl acetate increases.
- (3) The amount of free linalol decreases.
- (4) The total amount of linalol decreases.
- (5) The amount of terpenes increases.

The results obtained are shown in the following table :—

|   | Oil of        |              |
|---|---------------|--------------|
|   | Green fruits. | Ripe fruits. |
| Specific gravity at 14° . . . . .           | 0.882         | 0.883        |
| Specific gravity at 18° . . . . .           | 0.879         | 0.880        |
| Optical rotation, in 100 mm. tube . . . . . | + 14° 38'     | + 20° 30'    |
| Acidity, as acetic acid per cent. . . . .   | 0.289         | 0.283        |
| Linalyl acetate per cent. . . . .           | 33.8          | 38.2         |
| Free linalol per cent. . . . .              | 15.1          | 5.6          |
| Total linalol per cent. . . . .             | 41.7          | 35.6         |

Having established these results, it was of interest to study comparatively the terpene portions of the two essences, and then to consider the various observations all together.

Two hundred grams of each of the two products were saponified by boiling for one hour with a slight excess of alcoholic potash ; the saponified oils were then precipitated by the addition of water.

Their physical constants were then as follows :—

|   | Essence of    |              |
|---|---------------|--------------|
|   | Green fruits. | Ripe fruits. |
| Specific gravity at 16° . . . . .           | 0.8625        | 0.8615       |
| Optical rotation, in 100 mm. tube . . . . . | + 13° 52'     | + 20° 10'    |

## P E R F U M E R Y

Thus, the specific gravity of the oil of ripe fruits has diminished more than that of the oil from green fruits, as would be expected from its higher ester content.

The increase in the amount of linalyl acetate, accompanied by a decrease in the total linalol, indicates that the linalol appears in the plant tissues earlier than its ester. Further, the free acetic acid reacts with the linalol, producing esters on the one hand by esterification, and terpenes on the other hand by dehydration. Charabot draws from these facts the following practical conclusion. Oil of bergamot, having a value which depends almost entirely on its ester content, is best expressed from fruits which have arrived at complete maturity. Linalol is also the parent odour bearer in the essential oil of French lavender. Charabot examined the progressive development of this oil in the plant by distilling three samples of oil from the same plantation of flowers which were cut at intervals of a fortnight, the first in the budding stage, the second from the fully flowering plant, and the third from the flowers when they had faded. The three oils had the following characters . -

|                         | Buds.    | Flowers. | Faded<br>flowers. |
|-------------------------|----------|----------|-------------------|
| Specific gravity .      | 0.885    | 0.885    | 0.882             |
| Optical rotation .      | - 6° 32' | - 6° 48' | - 6° 50'          |
| Free acetic acid* .     | 0.52     | 0.47     | 0.38              |
| Esters per cent. .      | 36.6     | 40.4     | 39.8              |
| Free linalol per cent.  | 21.0     | 16.7     | 18.9              |
| Total linalol per cent. | 49.8     | 48.4     | 50.3              |

The acidity has therefore diminished as the flower develops ; the amounts of free and total linalol have diminished, and the amount of esters increased, as the flower develops, and as the flower fades the oil contains more linalol and less esters. Here then, as in the case of oil of bergamot, the process of esterification is accompanied by a decrease in the amount of free acid and of total linalol. There can be no doubt that the esters are the result of direct action between the acids and the alcohols. Oil of basil contains a considerable amount of linalol compounds, together with the phenolic compound estragol. The examination of this oil was made at four different stages of the plant's development.

\* Expressed as grams per litre of distillation water.

## PERFUMERY

*First stage.* The oil was distilled from the young plants before flowering, and compared quantitatively with the oil distilled from the plants at the *second stage*, the commencement of flowering. It was found that the percentage of essential oil in the green parts of the plant has undergone a diminution at the commencement of the flowering period, and the young inflorescence is actually richer in essential oil than the green parts of the plant. In the *third stage*, when flowering is quite advanced, the proportion of essential oil has sensibly diminished in the green parts of the flower, during the accomplishment of the functions of the inflorescence. To a smaller extent, the proportion of oil in the inflorescences themselves has also diminished. Thus, in spite of the increase in the size and number of the green leaves, the manufacture of essential oil has not been able to keep pace with its consumption by the inflorescence during the fecundation process. In the *fourth stage*, at the maturity of the seeds, and when the essential functions of the flower have been performed, it was found that the proportion of essential oil had increased in the green parts of the plant to a quantity above that which existed in the third stage, corresponding to advanced flowering, but had diminished in the dying inflorescence, and the plant has now become, as a whole, poorer in odorous compounds. It is therefore seen that the essential oil is already present in the young green plant, and accumulates to the greatest extent up to the commencement of the flowering period, and commences to disappear as the flowering period advances. But during this period, whilst the amount of oil diminishes in the green parts, it increases in the inflorescences, and this last-named state of things is reversed after fecundation is accomplished.

The examination of the essential oil of geranium is of special interest on account of the fact that the plant, at all events in the south of France, produces but few flowers, whilst the leaves, in which the perfume chiefly resides, are very abundant. (*Vide Roure-Bertrand Fils, Bulletin*, October, 1900.)

The odour is due, in the main, to a mixture of geraniol with a little citronellol in the free state, together with a considerable amount of esters of these alcohols, of which the typical one is geranyl tiglate. The ketone menthone is also present, and has some effect on the odour. Charabot distilled the green plants on July 18th, and a second cutting of the same group of plants—still green, a month later. The July sample had a specific gravity 0.897; optical rotation,  $-10^{\circ}$ ; esters, 5.8 per cent.; free



## P E R F U M E R Y

alcohols, 64 per cent. ; total alcohols, 67·8 per cent. ; and acid coefficient, 43·8. The August distillate had a specific gravity 0·899 ; optical rotation,  $-10^{\circ} 16'$  ; esters, 10 per cent. ; free alcohols, 62·1 per cent. ; total alcohols, 68·6 per cent. ; and acid coefficient, 41. Here again, the acidity decreases as the plant develops, and the amount of esters increases at the same time. The amount of total alcohols increases slightly, and that of the free alcohols decreases. It was found that no appreciable quantity of menthone was present in either oil, but when the plant was completely mature, an appreciable quantity of menthone appeared in the oil.

These facts, though without absolute signification, show, however, that the samples examined, *which had been prepared from green plants*, contained no menthone, or at all events, only very small quantities of it. A product obtained from the same crop, but prepared after the flowering and complete maturation of the plants, was quantitatively examined for menthone. The results obtained were as follows :—

|   |       |
|---|-------|
| Coefficient of saponification of the acetylated essence             | 200   |
| Coefficient of saponification of the reduced and acetylated essence | 213·1 |
| Coefficient of saponification corresponding to the menthone         | 13·1  |

These figures allow the conclusion to be drawn that *the ketonic constituent is produced principally at the period at which the plant possesses the greatest respiratory activity*. The result is therefore the same as in the case of ketones or aldehydes existing in the plant side by side with alcohols to which they correspond or from which they originate in the course of vegetation.

Finally, it was of interest to extract and examine comparatively the alcoholic portions of the essences studied. The method of Haller was applied, making use of a process differing slightly from that proposed by Erdmann and Huth (*Jour. Prakt. Chem.*, 2, 56, 1), and starting with 15 grams of each of the two essences. The results obtained were :—

|                                  | Weight of<br>alcohols extracted. | Rotatory power<br>in 100 mm. tube. |
|----------------------------------|----------------------------------|------------------------------------|
| Product collected on July 18th   | 7·5 grams.                       | .. $- 1^{\circ} 32'$               |
| Product collected on August 21st | 7·2 „                            | .. $- 2^{\circ} 12'$               |

The alcoholic portion of oil of geranium being composed almost exclusively of a mixture of geraniol, which is inactive, and of

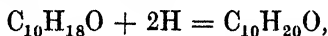
citronellol, which is lævorotatory, the more active product would therefore be richer in citronellol.

To prove whether the ratio between the proportion of geraniol and that of citronellol does vary during the vegetation, as the rotatory powers of the alcoholic portions would seem to indicate, the citronellol was isolated by the process described by Tieman and Schmidt (*Berichte*, 29, 903). Starting with 7 grams of each of the two alcoholic mixtures, there were obtained :—

|                                       |                            |
|---------------------------------------|----------------------------|
| From the oil collected on July 18th   | 1.23 grams of citronellol. |
| From the oil collected on August 21st | 1.97 „ „                   |

These observations show and confirm that *the proportion of citronellol in relation to that of the geraniol increases during vegetation.*

Can it be concluded that this increase of the citronellol in the essence takes place at the expense of the geraniol? This seems as yet hardly justifiable. Still, this transformation of geraniol into citronellol, according to the equation



would be quite conceivable, especially since it would take place in the green parts of the plant which are known to be strongly reducing media. This hypothesis would be in accordance, both with the observations of a chemical nature described above, and with the physiological data which we possess.

In order to ascertain whether the conclusions drawn from the above cases, namely, that the increase in the proportion of alcohols and esters in an essential oil should correspond with the most active period of the development of the green parts of the plant, applied to typical perennial plants, it was considered desirable to study a plant which, after a long period of slow vegetation, undergoes a rapid development and elaborates during this quick growth a considerable quantity of essential oil. This condition was, in fact, necessary in order that the quantity of terpene compounds formed might be greater than the quantity of the same substances after modification in the organs endowed with a powerful respiratory energy. *Artemisia absinthium* was chosen as lending itself well to such a study (*Roure-Bertrand Fils, Bulletin*, October, 1900).

The essential oil of absinthe contains, principally, a ketone, *thujone*,  $\text{C}_{10}\text{H}_{16}\text{O}$ , in considerable proportion, *acetic*, *valerianic* and *palmitic esters* of *thujol*, the alcohol corresponding to thujone, and *thujol*,  $\text{C}_{10}\text{H}_{18}\text{O}$ , in the free state.

## P E R F U M E R Y

On June 8th, 1899, after a period during which the plants had developed very slowly, a sample of essential oil was prepared; the yield amounted to 0.1429 per cent.

About a month later, on July 12th, the vegetation had reached its maximum activity; a fresh sample of essence was then prepared from plants in the same field; the yield in this case had increased to 0.2450 per cent.

Thus, during the period of active vegetation, not only had the weight of the individual plants increased considerably, but the relative proportion of essential oil was nearly doubled.

The following are the characters of the two oils :—

|  | June 8th.     | July 12th.     |
|--|---------------|----------------|
| Specific gravity at 24° . . . . .                  | 0.9307        | 0.9253         |
| Esters of thujol (calculated as acetate) . . . . . | 9.7 per cent. | 13.1 per cent. |
| Free thujol . . . . .                              | 9.0 „         | 9.2 „          |
| Total thujol . . . . .                             | 16.6 „        | 19.5 „         |
| Thujone . . . . .                                  | 43.1 „        | 35.0 „         |

The results of the estimations of the thujone and thujol were confirmed by analysing in both cases the fractions corresponding to these two bodies.

It will be seen that *during the period of active vegetation the essential oil becomes sensibly richer in esters of thujol, whilst the proportion of free thujol remains almost constant, and that of the total thujol increases.*

*During this same period a part of the thujol formed is converted into thujone, but this transformation is less than during the period of slow vegetation, so that the proportion of thujone expressed as per cent. of the essence has diminished.*

During the period under consideration, the period of active vegetation, it is seen that not only does the weight of the plant increase considerably, but also the relative proportion of essential oil attains a value almost double that in the former stage. A considerable quantity of thujol has been formed. The brilliant light, whilst it has diminished the respiratory activity, has at the same time increased the energy of the function of assimilation. The two effects have so combined that the resultant of the two functions is far more in favour of assimilation than in the preceding period. The quantity of oxygen fixed by the plant then becomes

## P E R F U M E R Y

insufficient to convert so large a proportion of thujol into thujone as during the period of slow vegetation. The result is that the proportion of thujone, expressed in terms of 100 parts of essence, is smaller in the second stage than in the first. On the other hand, the proportion of thujol increases during the period of active vegetation. As for the esterification, it follows the normal course.

When the flower has performed its function, the oil commences to return to the green parts of the plant, as in the case of basil oil.

In regard to the menthol group, for which study oil of pepper-mint was obviously chosen, the investigation was extended so as to include the effect of manuring on the evolution of the terpene and other compounds. In the first place, the oils examined for the purposes of comparison were four in number, namely, (1) oil distilled from quite young plants, about 20 inches in height, in which the inflorescence has just formed; (2) oil distilled from the plants when the buds were commencing to appear, and from which the inflorescences were removed; (3) oil distilled from the inflorescences so removed; (4) oil distilled from the normal well-developed plant when the flowers were fully formed. These four oils had the following characters:—

|                                    | 1.           | 2.       |
|------------------------------------|--------------|----------|
| Specific gravity . . . . .         | 0.9025 ..    | 0.9016   |
| Optical rotation . . . . .         | — 24° 10' .. | — 26°    |
| Esters per cent. . . . .           | 3.7 ..       | 10.3     |
| Combined menthol per cent. . . . . | 2.9 ..       | 8.1      |
| Free menthol per cent. . . . .     | 44.3 ..      | 42.2     |
| Total menthol „ . . . . .          | 47.2 ..      | 50.3     |
| Menthone „ . . . . .               | 5.2 ..       | 4.2      |
|                                    | 3.           | 4.       |
| Specific gravity . . . . .         | 0.9081 ..    | 0.920    |
| Optical rotation . . . . .         | — 20° 15' .. | — 2° 37' |
| Esters per cent. . . . .           | 7.5 ..       | 10.7     |
| Combined menthol per cent. . . . . | 5.9 ..       | 8.4      |
| Free menthol per cent. . . . .     | 29.9 ..      | 32.1     |
| Total menthol „ . . . . .          | 35.8 ..      | 40.5     |
| Menthone „ . . . . .               | 16.7 ..      | 10.2     |

So that there is an increase in esters in the total essential oil (as calculated from 2 and 3 combined) distilled from the whole of the plant as the green part develops. The alcohol (menthol) has decreased during the development of the inflorescences, whilst

the menthone has increased. Hence the oil obtained from plants systematically deprived of their inflorescences contains but a small quantity of menthone, but is rich in free menthol and in esters. The formation of menthyl esters takes place principally in the green portions of the plant, whilst the menthone is produced principally in the flowers.

It is thus clear that at the beginning of vegetation the oil is rich in menthol, nearly all of which is present in the free condition, only a small percentage of esters being present. Only a small quantity of menthone is present. As the green parts of the plant develop the esters increase, as is the case with other oils. As the essential oil reaches the inflorescence the esters commence to diminish, but if the whole plant be distilled, the esters have increased owing to the continued growth of the green parts, which more than balances the decrease in the inflorescence. Menthone increases as the flowers develop, and this point is well emphasised by the fact that in the diseased mint (*menthe basiliquée*), where the flowers no longer appear, the oil is practically free from menthone. The effects of manuring the peppermint plants with sodium nitrate are elaborately recorded by Charabot and Hébert (*Roure-Bertrand Fils, Bulletin*, October, 1902). The following were the conditions of cultivation and percentages of oil obtained :—

*July 18th, 1901.*—The inflorescences were clearly defined and the flowers were not yet entirely opened. Four rows of plants cultivated normally were cut, weighing 14 kg., which yielded 23·47 grams of oil (yield, 0·1676 per cent.).

*July 24th.*—Abundant flowering. Two rows cultivated normally gave 11·5 kg. of plants, and these gave 23·42 grams of oil (yield, 0·2036 per cent.). Two rows cultivated with sodium nitrate contained 11·5 kg. of plants, which gave 23·18 grams of oil (yield, 0·2017 per cent.).

*August 20th.*—Complete maturity. In order to compare the oils contained in the chlorophyll-bearing organs, the inflorescences and the violet-tinted lower portions of the stems were separated. One row cultivated normally, weighing 6 kg., gave 3 kg. of chlorophyll-bearing material, from which were obtained 0·921 gram of oil (yield, 0·033 per cent.). One row and a half cultivated with sodium nitrate weighed 8·5 kg., and gave 4 kg. of chlorophyll-bearing material containing 1·867 grams of oil (yield, 0·047 per cent.).

*September 16th.*—After the fall of the petals and the partial withering of the inflorescences. Nine rows cultivated normally

## P E R F U M E R Y

gave 34.9 kg. of plants and 114 grams of oil (yield, 0.356 per cent.). One row and a half *cultivated with sodium nitrate* gave 7 kg. of plants and 20.2 grams of oil (yield, 0.289 per cent.).

The analysis of the essential oils, extracted under the conditions enumerated above, yielded the results set forth below.

*Rotatory Power, Esters of Menthol.*—The estimation of the esters was carried out with such precautions that any difference exceeding 0.2 per cent. should be regarded as real.

|   | July 18th, 1901.<br>Beginning of<br>the flowering. | July 24th, 1901.<br>During the flowering. |  |
|---|--|---|--|
|   | Normal<br>cultivation.                             | Normal<br>cultivation.                    | Cultivation<br>with sodium<br>nitrate. |
| Rotatory power at 20° . . . . .                     | — 3° 30'   | — 3° 38'                                  | — 0° 10'                               |
| Esters (calculated as menthyl<br>acetate) . . . . . | 8.8 per cent.                                      | 12 per cent.                              | 12.3 per cent.                         |
| Combined menthol . . . . .                          |  | 9.5 „                                     | 9.7 „                                  |

|   | August 20th, 1901.<br>Chlorophyll-bearing<br>portions. | September 16th, 1901.<br>After the fall of the<br>petals. |  |
|---|--|---|--|
|   | Normal<br>cultiva-<br>tion.                            | Cultiva-<br>tion with<br>sodium<br>nitrate.               | Normal<br>cultiva-<br>tion.      Cultiva-<br>tion with<br>sodium<br>nitrate. |
| Rotatory power at 20° . . . . .                     |  |   | — 5° 30'      — 2° 30'   |
| Esters (calculated as menthyl<br>acetate) . . . . . | 33.3 per<br>cent.                                      | 39.2 per<br>cent.   | 27 per<br>cent.      28.9 per<br>cent.                                       |
| Combined menthol . . . . .                          | 26.2 per<br>cent.                                      | 30.9 per<br>cent.   | 21.3 per<br>cent.      22.8 per<br>cent.                                     |

It will be noticed that *the plant cultivated in a soil to which sodium nitrate has been added elaborates the essential oil constantly richer in esters than that obtained by normal cultivation.* The difference is very marked, and attains 5.9 per cent. in the green portions.

*Free Menthol and Total Menthol.*—Estimation of the menthol

# **P E R F U M E R Y**

by successive acetylation and saponification yielded the following numbers :—

|   | July 18th, 1901<br>Beginning of<br>the flowering. | July 24th, 1901.<br>During the flowering |  |
|---|---|--|--|
|   | Normal<br>cultivation.                            | Normal<br>cultivation.                   | Cultivation<br>with sodium<br>nitrate. |
| Free menthol in the original<br>oil . . . . . | 31.1 per cent.                                    | 28.7 per cent.                           | 27.1 per cent                          |
| Total menthol . . . . .                       | 41.1 "  | 38.2 "                                   | 36.7 "                                 |
| Combined menthol . . . . .                    | 17 "  | 24.8 "                                   | 26.2 "                                 |
| Total menthol . . . . .                       | 100   | 100                                      | 100                                    |

September 16th, 1901.  
After the fall of the petals.

|                                  | Normal<br>cultivation. | Cultivation with<br>sodium nitrate. |
|----------------------------------|------------------------|-------------------------------------|
| Free menthol in the original oil | 25.7 per cent.         | 23.0 per cent.                      |
| Total menthol . . . . .          | 47 "                   | 45.8 "                              |
| Combined menthol . . . . .       | 47.4 "                 | 49.8 "                              |
| Total menthol . . . . .          | 100                    | 100                                 |

It will be observed that the addition of sodium nitrate to the soil has brought about a slight decrease in the proportion of total menthol. In spite of this decrease, the quantity of combined menthol was greater in the case of the cultivation with sodium nitrate, so that this salt is really proved to be favourable to the esterification.

*Menthone.*—The averages of the results obtained from several series of determinations are summed up in the table below.

|          | July 18th, 1901<br>Beginning of the<br>flowering. | July 24th, 1901.<br>During the flowering.              |                                     |
|----------|---|--|-------------------------------------|
|          | Normal<br>cultivation.                            | Normal<br>cultivation.                                 | Cultivation with<br>sodium nitrate. |
| Menthone | 4 per cent.                                       | 8.2 per cent.  | 6 per cent.                         |
|          |   | September 16th, 1901.<br>After the fall of the petals. |                                     |
|          |   | Normal<br>cultivation.                                 | Cultivation with<br>sodium nitrate. |
| Menthone |   | 2.5 per cent.  | 2.5 per cent.                       |

The addition of sodium nitrate to the soil, therefore, has the effect of decreasing the proportion of menthone. This diminution, however, is less marked than in the case of sodium chloride, but it does actually take place. In fact, the oil extracted on July 24th from the plants cultivated normally contains 8.2 per cent. of menthone, whilst that obtained from the plants cultivated with sodium nitrate contains only 6 per cent. On September 16th, operating on plants bearing withered inflorescences which had lost their petals, the figures obtained showed no difference; however, seeing that the proportion of menthone under these conditions is very small, and that the estimation of this body is not very accurate, conclusions can only be based upon the figures obtained from the plants harvested on July 24th.

It would appear to follow from this result, and from that obtained in the previous study, that the causes which are favourable to esterification tend, on the other hand, to hinder the oxidation of the alcoholic principle.

*Conclusions.*—The principal facts established by the work just described are as follows:—

*Under the influence of sodium nitrate the percentage increment of the organic matter in the plant is accentuated, the relative loss of water increases, the esterification is favoured, the elaboration of the menthol and the transformation of this alcohol into menthone, on the other hand, are retarded.*

It is well to add that the sodium nitrate is favourable to the production of oil (computed per acre).

The comparison of the essential oils in the orange plant is of considerable interest. If the oil be distilled from the flowers, it is found to be rich in oxygenated constituents, including esters, so that it is easily soluble in alcohol. If the flowers are fertilised and the fruit allowed to develop to the size of about a full-grown pea, and the oil distilled from them, the oxygenated constituents have become considerably less in amount, the hydrocarbons (terpenes) have increased, and the oil is much less soluble in alcohol. If the fruit is allowed to mature, the essential oil, which now resides entirely in the peel of the orange, is almost entirely composed of terpenes, with only a small amount of oxygenated constituents, and the oil is only slightly soluble in alcohol. To sum up the general conclusions obtained and indications pointed out by the foregoing experimental work, it is clear that the odiferous material first appears in the young green organs of the plant. It continues to be formed, and accumulates up till the time



of flowering, and passes from the leaves through the stem and thence to the inflorescence, obeying the usual laws of diffusion and osmotic pressure when in aqueous solution. As such aqueous solution reaches organs containing saturated solutions of the perfume materials, and water evaporates, the perfume material is, *pro tanto*, precipitated, the remaining portion still moving freely by diffusion, and reaching those parts of the plant where it is required, principally the inflorescence. When the flower is performing its essential function, namely, fecundation, a certain amount of essential oil is consumed in the flower itself. The green parts are in all probability producing more essential oil during this period of consumption. The practical result, however, is a net loss in essential oil during the fertilisation of the flower and maturing of the fruit (except where the fruit itself is rich in essential oil). As a result it is usually advisable that perfume-bearing plants should be harvested before fertilisation takes place. When this is accomplished, the oil usually commences to redescend into the stem and organs other than the flower. The odoriferous substances are able to circulate in the plant in aqueous solution, and can be precipitated at those points which are termed secreting cells, glands or vessels, etc. It is in consequence of these facts that Charabot and his pupils disagree with the views of Tschirch and his fellow-workers as to the so-called resinogenous layer.

The German botanist Von Marilaun has devoted a good deal of attention to the relationship of the perfume of the plant to the attraction of insects for the purpose of fertilisation, and although his views do not appear to be based on sound chemical knowledge, they are nevertheless entitled to attention. Von Marilaun (see *P. & E. O. R.*, 1917, 294) has divided the floral perfumes into five groups—namely, the indoloid, aminoid, paraffinoid, benzenoid, and terpenoid groups. Taking the so-called indoloid group of perfumes, which includes such bodies as skatol and indol, it is a fact that many of the flowers possessing this type of odour, including many orchids and aroids, yield essential oils whose odours are quite revolting, sometimes recalling that of decomposing flesh or even rotten fish. It is a strange fact that flowers having this type of odour very frequently are so marked with livid spots, violet streaks and reddish brown veins, that they bear a marked resemblance to small animal corpses in appearance as well as in odour. It is hardly to be doubted that in these cases the odour is entirely protective in function.

Coming to Von Marilaun's aminoid perfumes, which are based on amines, including trimethylamine, there can again be little doubt that the perfume is entirely protective in function, and that the odour of these derivatives of ammonia is found to be highly objectionable to most animal life, except to the particular group of insects who frequent the flowers for the sap and so effect fertilisation.

Von Marilaun's division, the "benzenoid scents," is not a very happy one, as it embraces every shade of odour which can be referred to the benzene nucleus as its parent hydrocarbon, besides some which have no relationship whatever with that substance, nor would a chemist with any knowledge of essential oils subscribe to all his views as to the "paraffinoid scents."

There is one thing which strikes the careful observer as very remarkable. Honey may have a very different flavour and odour according to the flowers from which the bees have collected the saccharine sap. But practically all honeys, however different in perfume, have an underlying odour which is common to them all, and which may be termed the "honey" odour. This is so similar to the odour of synthetically produced phenyl-acetic acid that one can scarcely doubt that it is due to this body. So that it would seem that either phenyl-acetic acid, or a substance which is easily converted into that body by the bee, is the particular perfume which attracts the bee to collect the saccharine exudation of the flower and to fecundate the plant at the same time.

It is true that many flowers emit a perfume by day which is different from that which is emitted during the night. How far this is to be explained by the types of insect which are liable to visit the plant by day and by night respectively one cannot say. But it may be that the day visitor is harmless and attracted by the day perfume, and the night visitor harmful and repelled by an objectionable scent.

Comparative anatomical studies show an enormous difference between the olfactory organs of human beings and of animals, so that the perception of perfumes may be, and indeed must be, very different in many animals from what it is in the human being. There is every reason to believe that the olfactory nerves of many insects are very susceptible to some perfumes, whilst totally unable to perceive others. For example, the flowers of the ordinary Virginian creeper are green, and can have no colour attraction to insects. To the human nose, too, they are odourless, and yet bees fly to them from considerable distances in such a

## PERFUMERY

way as to indicate that the attraction is entirely a question of smell. Another example cited by Von Marilaun is that of *Bryonia dioica*. The flowers are staminate on one plant, and pistillate on another, and the pollen is not powdery, so that insect fertilisation is necessary. The flowers, especially the female ones, are green and insignificant, and half hidden under the foliage. Many insects fly past them without noticing them at all, and they are almost exclusively visited by one of the *Hymenoptera*, namely, *Andrena florea*, which can find these flowers even in the most out-of-the-way places. It must therefore be assumed that the perfume of this particular flower can be perceived by this particular insect, and not by others. There are many other plants whose flowers, to the human nose, are odourless, but which, although quite insignificant in colour and appearance, attract certain insects, and only them, apparently, on account of a perfume which they alone can perceive. Popularly speaking, these various considerations lead to what is known as "flower fidelity," the true extent of which can scarcely be established at present with the limited powers of observation at our disposal.

Some of the indoloid scents, which are to be described generally as objectionable, have a marked attraction for certain flies of the classes *Scatophaga*, *Sarcophaga* and others, which are to be found on carrion and excreta, whilst they present no attraction to the butterfly or bee. Many aminoid scents attract beetles and some of the *Hymenoptera*, but never, apparently, butterflies. But it appears that no insect which is attracted by an aminoid perfume pays any attention to the honey odour. Butterflies never even pause near a flower having the particular type of odour associated with honeysuckle, and do not appear to be able to perceive it.

Von Marilaun has recorded the following examples of the power of insects to perceive odours at a distance. Some years ago the aroid plant *Dracunculus creticus*, from Cyprus, was planted on the edge of a small group of coniferous plants in the Vienna Gardens of Botany. No refuse, manure, or similar decomposing matter was present anywhere near, nor were any flies or beetles of the type that are attracted by dung or carrion known to be anywhere in the neighbourhood. During the summer the large bell-shaped flowers of the aroid plant opened, and immediately carrion flies and dung beetles arrived from all directions. The peculiar indol-like perfume was only noticeable a few yards off by human beings, but the insects must have come from many hundreds of yards to the flowers, attracted by their perfume.

but also that it is the heat rays that decompose it the more readily.

• In 1893, Timiriacheff ("Actions photochimiques des rayons extrêmes du spectre visible," Moscow, 1893) stated that "the action of the rays of the red part of the spectrum is much more energetic than the others on the chlorophyll function," and concluded that "chlorophyll acts as a screen to absorb the heat rays of the solar spectrum, being necessary to it for the decomposition of the carbon dioxide, whilst other rays pass to the plant for the development of certain substances." This conclusion is the starting point of Canals' investigation.

Some young plants of thyme (*Thymus vulgaris*) from the waste lands in the neighbourhood of Montpellier were gathered, using every precaution to obtain as much of the roots as possible. They were taken at once to the Institut de Botanique de Montpellier and were replanted in pots.

The pots were carefully watered and were left in the open air for a few days until the plants took root. The living plants were divided into three lots. The first lot was placed in a frame of ordinary transparent glass; the second in a neighbouring frame with red glass, and the third also in a neighbouring frame, but with blue glass.

The colour of the glasses was not selected at hazard. Canals had previously examined spectroscopically a whole series of coloured glasses and had fixed his choice on two, one red and the other blue, which only allowed to pass rays of known wavelength. The red glass allowed the passage only of rays of the following wavelengths. —

$$\lambda - 0\mu 7800 \text{ to } \lambda = 0\mu 6060,$$

whilst the blue ones allowed the passage of rays of wavelength

$$\lambda - 0\mu 5820 \text{ to } \lambda = 0\mu 4045.$$

It is seen that only the two extremities of the visible spectrum were used, that is to say, he employed the group of heat rays and the group of rays with chemical action.

After being in the frames for four days, one could observe that the first lot were beginning to flower (colourless glass), in the other two lots everything appeared to be stationary.

Five or six days later the flowers in the first lot were present in great numbers, the stems being quite upright and of medium length. They appeared to be in no way incommoded by their stay in the frame. It was noted, however, that the leaves were a

## P E R F U M E R Y

little larger than those that continued to grow on the waste land. The other two lots already showed signs of trouble. Under blue glass the stem remained upright, though a little longer than those in the first frame, but there were no flowers. Under red glass the stems were of exaggerated length, and fell without strength on the edges of the pot. The extremities of the stems of some of the plants were dead, but the remainder were, although still green, without flowers.

Ten days afterwards, that is to say, twenty days after the commencement of the experiments, the following results were noted: the plants of the first lot were all in flower, none dead among them, but they showed some difference from the thyme growing in the open air. The colour of the flowers was paler, the stems were longer, the leaves of a more delicate green, and above all their limb was larger.

In the lot submitted to the action of the chemical rays, the greater part of the plants were in flower, some were dead, but the general aspect of the plants seemed identical with that of the preceding.

Those submitted to the action of the red rays had undergone great modification. Quite at first, flowering was impossible, some very few flowered, but two or three flowers only per plant could be counted. Numerous plants were dead, and the survivors possessed stems of excessive length and very large leaves. The xerophile character of the thyme had completely disappeared.

At this point the flowering ends and the stems were gathered, which were distilled with steam in order to extract the essential oil.

The thymol was determined by the method which consists in treating with alkali and then converting the thymol into biiodo-thymol with the aid of iodine. By adding a known excess of iodine, it is sufficient to titrate against standard hyposulphite to obtain the quantity of iodine combined with the thymol, from which the proportion of thymol contained in the oil can be calculated.

The figures thus obtained were as follows:—

|                             | Thymol.<br>Per cent. |
|-----------------------------|----------------------|
| Essential oil (red glass) . | 25.5                 |
| „ (blue glass) .            | 36                   |
| „ (colourless glass) .      | 45                   |
| „ (waste-land) .            | 52.5                 |

## P E R F U M E R Y

Consideration of the whole of these results seems to allow of the following conclusions :—

(1) The quantity of thymol in the oil diminishes in proportion as the xerophil character of the plant is attenuated.

(2) Chemical rays have a detrimental effect on the formation of thymol.

(3) Heat rays have a still more detrimental action.

**PERGULARIA.**—A number of species of *Pergularia*, a genus belonging to the natural order *Asclepiadaceæ*, are cultivated in China and the East Indies on account of the great fragrance of their flowers. They are mostly climbing shrubs, inhabiting India, China, Madagascar, and the Moluccas. The flowers are greenish or yellowish, and are very highly scented. The principal species are *P. odoratissima*, *P. acedens*, *P. minor*, and *P. parviflora*. The perfume is not extracted.

**PERILLA OIL.**—The plant *Perilla* was first described by Loureiro in his "Flora of Cochinchina" in 1790, and definitely given generic rank by Decaisne in 1852. There are three species of perilla which are of particular interest.

The dried leaves of *Perilla citriodora* yield from 2 to 3 per cent. of essential oil of specific gravity 0.911 to 0.913, which contains about 60 per cent. of citral. Kondo and Yamaguchi (*Jour. Pharm. Soc. Japan*, 1919, **446**, 263) have isolated from it a compound of the formula  $C_{10}H_{14}O$ , which they have named perillene.

*Perilla ocymoides* grows in the mountains of northern India, and is known in China as *Pe-sow*. It is used as a flavouring agent.

*Perilla arguta*, indigenous to China and Japan, is known in Japan as *shiso*. Its leaves yield an essential oil having the following characters :—

|                  |   |   |       |                |
|------------------|---|---|-------|----------------|
| Specific gravity | . | . | .     | 0.926–0.939    |
| Optical rotation | . | . | .     | — 90° to — 93° |
| Refractive index | . | . | .     | 1.4983         |
| Aldehydes        | . | . | about | 50 per cent.   |

The oil contains perillic aldehyde, and probably esters of geraniol. Gattefossé has examined the oil, and considers it may be of value in perfumery. Its odour somewhat recalls that of hay. Perillic aldehyde was described by Semmler and Zaar as dihydrocuminic aldehyde (*Berichte*, 1911, **44**, 52), but it is now known that the two bodies are identical.

**PERILLIC ALCOHOL.**—See also "Dihydrocuminic Al-

## P E R F U M E R Y

cohol" This alcohol, of the formula  $C_{10}H_{16}O$ , is obtained by the reduction of perillic aldehyde, an aldehyde occurring in the oil of *Perilla nankinensis*. It has the following characters —

|                   |               |
|-------------------|---------------|
| Specific gravity  | 0.969 at 20   |
| Boiling point     | 120° at 11 mm |
| Refractive index  | 1.4996        |
| Specific rotation | — 68.5°       |

**PERILLIC ALDEHYDE.**—See also "Dihydrocuminic Aldehyde" —This body is present in the essential oil of *Perilla nankinensis*. It has the formula  $C_{10}H_{14}O$ , and has the following characters —

|                   |               |
|-------------------|---------------|
| Specific gravity  | 0.9617 at 18  |
| Boiling point     | 105° at 10 mm |
| Refractive index  | 1.50746       |
| Specific rotation | — 146°        |

It yields an oxime melting at 102°. On reduction with sodium, dihydropericlic acid  $C_{10}H_{16}O_2$  results, and the methyl ester of this acid yields dihydropericlic alcohol by further reduction with sodium. This is an oil with a rose odour and having the following characters —

|                  |               |
|------------------|---------------|
| Specific gravity | 0.9254 at 19  |
| Boiling point    | 115° at 10 mm |
| Optical rotation | $\pm 0^\circ$ |
| Refractive index | 1.4819        |

**PERSEA GRATISSIMA, OIL OF.**—The bark of *Persea gratissima*, a tree indigenous to tropical America, belonging to the natural order *Lauraceæ*, yields about 3 to 4 per cent. of essential oil of specific gravity about 0.970 and optical rotation about — 1°. The oil contains anethol and methyl chavicol. The leaves yield an essential oil which has a marked odour of tarragon. It has the following characters. —

|                                |               |
|--------------------------------|---------------|
| Specific gravity               | 0.955–0.962   |
| Optical rotation               | + 2° to + 3°  |
| Refractive index               | 1.5120–1.5150 |
| Ester number                   | 2–4           |
| Ester number after acetylation | 18–22         |

The North American tree, *Persea pubescens*, known as "swamp bay," is of interest in that its leaves yield about 0.2 per cent. of essential oil, which has been examined by Rabak (*U.S. Dept. of Agriculture, Bureau of Plant Industry Bulletin*, 1912 **235**, 20). It

found it to contain free butyric acid, and butyric, valerianic, and cœnanthylic acids in the form of esters. Camphor, eucalyptol, and probably borneol, are also present. The oil has a specific gravity about 0.935; optical rotation,  $+22^{\circ}$ ; refractive index, 1.5130; and ester value after acetylation, 18 to 22.

**PETITGRAIN OIL.**—The oil known as petitgrain oil without further qualification, is the oil distilled from the leaves and young shoots of the bitter orange tree, *Citrus Bigaradia*. The immature fruits are to a small extent unavoidably mixed with the leaves and twigs, but where any quantity of them are present the oil is of poor quality, and the physical characters and odour are so altered that the oil cannot then be properly described as pure petitgrain oil. At one time this oil was produced mainly in the south of France, where the finest oil is still distilled. A certain amount is distilled in Algeria, and a trifling amount in Spain. The French botanist Balanza went to Paraguay in 1873 and introduced the distillation of the oil there. At first the quality was poor, but it gradually improved, and is to-day of excellent quality; and as in France the results of pruning only are now distilled, whilst in Paraguay the whole tree is usually cut down and the distillation material selected from it, the Paraguay is often preferred to the French oil. Naturally, the Paraguayan method leads to a gradual extinction of the plant, and the practice is now being somewhat modified and controlled. Von Fischer-Treuenfeld ("Paraguay in Wort und Bild," Berlin, 1906, p. 187) states that, "although wild orange groves are still numerous, they are, because of the pernicious methods practised, remote from the inhabited places. The harvest is carried on all the year round, but principally from October to April. The leaves and young fruits are distilled on the spot, the wood being used as fuel. Thus indolence and vandalism have led to the annihilation of the orange fruits. More recently the Government has endeavoured to prevent the chopping down of the trees, and to regulate the harvesting by law. Hence the price of the oil has risen, and it is more and more difficult to obtain the product."

There are thirty to forty distilleries at work on this oil, and the production extends to 35,000 kg. or more annually when the crop of distilling material is favourable.

The quality of the oil exported is usually very good. This appears to be due to some extent to the fact that there is an expert attached to the collective purchasing bureau, who exercises control, with regular analyses, over the oil offered for sale.



## P E R F U M E R Y

The distillation is carried out in small factories of very simple construction, which are situated near creeks flowing through the orange grove. Owing to a practically total absence of any rapid methods of communication, it is impossible to centralise the industry. The hut in which the distillation takes place is covered with palm leaves. The apparatus consists of a boiler, a still, a condenser, and Florentine flasks for the collection of the oil. The boilers are heated by wood fires, and they are worked at very low pressure. The stills are primitive, somewhat resembling the ambulatory stills used in the Alps by peasant distillers. The distillation lasts thirty six hours, and about 0.3 to 0.4 per cent. of oil is obtained.

The woods are timber forests in which is an undergrowth of smaller trees amongst which orange trees occur in patches. These patches are termed *manchons*. In some places the bitter orange predominates, but in others there is an admixture with sweet orange trees and a variety known as *assessu*.

The small distillers usually receive advances in goods, foodstuffs, etc., at the commencement of the distilling season, and when the oil is tendered to the buyer for the associated purchasers, any adulterated parcel is at once rejected, so that effective control on the purity of the oil exists at the source.

Distilleries have been erected and the industry is in progress in the islands of the Parana, the river which in its upper course is called the Paraguay and lower down becomes the Parana. This river rises in the plateau of Matto Grosso, and the islands in question form the delta of the river as it throws itself into the estuary of the "River Plate." These islands enjoy a very temperate climate and are the healthiest part of the whole province of Buenos Aires. Oranges, lemons, mandarins, and many other fruit trees flourish here, and the leaves and twigs of the orange are being distilled. French petitgrain oil has the following characters —

|                  |                |
|------------------|----------------|
| Specific gravity | 0.889–0.8968   |
| Optical rotation | — 1° to — 8°   |
| Esters           | 50–70 per cent |

Eight petitgrain oils distilled by Charabot and Pillot (*Bull. Soc. Chim.*, 1898, iii, 19, 853, 1899, 21, 74) had the following characters —

|                  |                      |
|------------------|----------------------|
| Specific gravity | 0.891–0.8937         |
| Optical rotation | — 4° 45' to — 6° 15' |
| Esters           | 51.5–69.6 per cent   |

## P E R F U M E R Y

Normal Paraguay petitgrain oil has the following characters :—

|                            |                 |
|----------------------------|-----------------|
| Specific gravity . . . . . | 0.885–0.901     |
| Optical rotation . . . . . | – 3° to + 6°    |
| Refractive index . . . . . | 1.4590–1.4648   |
| Esters . . . . .           | 35–60 per cent. |

Most oils are soluble in 3 to 4 volumes of 70 per cent. alcohol. If, however, more than a very small proportion of the small unripe fruits are present in the distillation material, the oil may have an optical rotation up to + 10°, and may not be quite clearly soluble in 4 volumes of 70 per cent. alcohol, on account of the presence of terpenes. If an oil have a higher optical rotation than + 11°, it should be regarded as containing an excessive amount of terpenes, due to the distillation of an excessive amount of the young oranges.

A sample of petitgrain oil distilled in Jamaica was examined at the Imperial Institute (*Bull. Imp. Inst.*, 1913, 11, 437) and found to have the following characters :—

|                            |                 |
|----------------------------|-----------------|
| Specific gravity . . . . . | 0.8884          |
| Optical rotation . . . . . | – 6° 45'        |
| Total alcohols . . . . .   | 87.25 per cent. |
| Free alcohols . . . . .    | 31.6 ..         |

Its high lævorotation, as in the case of some French oils, may be due to the use of leaves only as the distillation material.

The following characters are given by *Schimmel & Co.* for petitgrain oils of various origins :—

|                         | Specific gravity. | Optical rotation. | Esters. Per cent |
|-------------------------|-------------------|-------------------|------------------|
| Calabria . . . . .      | 0.8746            | + 18°             | 26.3             |
| Spain . . . . .         | 0.8849            | + 8° 25'          | 28.6             |
| Comoros . . . . .       | 0.8664            | + 42° 45'         | 10.9             |
| Jamaica . . . . .       | 0.8846            | – 6° 30'          | 28.7             |
| West Indies . . . . .   | 0.8531            | + 43° 36'         | 2.1              |
| South America . . . . . | 0.887             | + 2°              | 36.5             |
| Syria . . . . .         | 0.8857            | – 3° 24'          | 27.1             |

It is obvious that the Comoros and West Indian samples were in the main orange oil, and not entitled to the name petitgrain oil.

Petitgrain oil contains traces of pyrrol and furfural. It contains camphene, pinene, limonene, and dipentene. Linalol and

## P E R F U M E R Y

geraniol, both free and in the form of esters, are present as well as nerol and terpineol. Traces of methyl anthranilate are also present.

The following allied oils may here be described.

Two oils distilled in southern France from the leaves of the sweet orange tree ("Petitgrain Portugal") had the following characters :—

|                  |           |           |    |           |
|------------------|-----------|-----------|----|-----------|
| Specific gravity | . . . . . | 0.8602    | .. | 0.8584    |
| Optical rotation | . . . . . | + 56° 46' | .. | + 53° 52' |

An Algerian oil was found to have a specific gravity 0.8705; optical rotation, + 21° 33'; and ester content, 21.6 per cent. (*Jour. de Pharm. et de Chim.*, 1909, vi., 30, 484). This oil contains camphene, limonene, citral, geraniol, and probably linalol.

The oil distilled from the leaves, twigs and immature fruits of the lemon tree (*Citrus limonum*) is known as *Petitgrain citronnier*. It has an odour resembling that of ordinary petitgrain, but also recalling that of lemon. It has the following characters :—

|                  |           |                 |
|------------------|-----------|-----------------|
| Specific gravity | . . . . . | 0.868–0.894     |
| Optical rotation | . . . . . | + 14° to + 35°  |
| Ester number     | . . . . . | 14–46           |
| Aldehydes        | . . . . . | 20–30 per cent. |

The oil contains limonene, citral, and geraniol, and probably camphene and linalol.

Jeancard and Satio give the following figures for a sample examined by them :—

|                  |           |                 |
|------------------|-----------|-----------------|
| Specific gravity | . . . . . | 0.8768          |
| Optical rotation | . . . . . | + 13° 20'       |
| Esters           | . . . . . | 12.25 per cent. |

Mandarin petitgrain oil, distilled from the leaves of *Citrus madurensis*, is very variable in characters. A Spanish oil described by *Schinmuel & Co.* (*Report*, October, 1902, 83) was of a yellow colour with a blue fluorescence. It had a specific gravity 1.0142; optical rotation, + 7° 56'; and ester number, 216. Oils distilled in the south of France had the following characters :—

|                  |                    |             |
|------------------|--------------------|-------------|
|                  | 1.                 | 2.          |
| Specific gravity | . . . . . 1.005    | .. 1.0643   |
| Optical rotation | . . . . . + 7° 19' | .. + 2° 20' |
| Ester number     | . . . . . 159      | .. 265      |

Charabot (*Comptes Rendus*, 1902, 135, 580) describes a sample which had an optical rotation + 6° 40' and contained about 50 per cent. of the methyl ester of methyl-anthranilic acid.

## PERFUMERY

Hesse (*Chem. Zeit.*, 1903, 2, 497) distilled 250 kilos of leaves in the south of France, and obtained 618 grams of "light" essential oil which floated on the surface of the distillation water, and 159 grams of heavy oil which sank to the bottom. The light oil had a specific gravity 0.993; optical rotation,  $+5^{\circ}42'$ ; and contained 55.7 per cent. of methyl methyl-anthranilate. The heavy oil had a specific gravity 1.033; optical rotation,  $+3^{\circ}20'$ ; and contained 67.65 per cent. of methyl methyl-anthranilate.

The oil distilled from the leaves of *Citrus medica* (lime leaves) in Dominica was found by Schimmel & Co. (Report, October, 1910, 79) to have a specific gravity 0.8783; optical rotation,  $+37^{\circ}30'$ ; and ester number, 23. An oil from Montserrat examined at the Imperial Institute (*Bull. Imp. Inst.*, 1913, 11, 436) was found to have similar characters. This oil contains dipentene, and possibly the ketone methyl-nonyl ketone.

An oil distilled from the small immature orange fruits (about the size of green peas) has been examined by the writer, and found to have a specific gravity 0.852, and an optical rotation  $+75^{\circ}$ . It contains methyl anthranilate and a pyrrol compound, besides a large quantity of terpenes.

The writer has also examined an oil distilled from lime flowers (*Chemist and Druggist*, 1900, 56, 993). This oil had a specific gravity 0.870, and optical rotation  $+21^{\circ}30'$ . It contained linalol and methyl anthranilate.

**PHALEROCARPUS.**—*Phalocarpus serpyllifolia* is a native of North America from Canada to Pennsylvania. It is known as the wild thyme-leaved snowberry. It has the same odour and taste as the well-known wintergreen, but is not distilled for oil, as apparently other plants, such as the sweet birch, are more economical for the purpose.

**PELLANDRAL.**—This body is an aldehyde of the formula  $C_{10}H_{16}O$ , found in the essential oil of water fennel. It is a liquid having an odour recalling that of oil of cummin. It has a specific gravity 0.9445; optical rotation,  $-36^{\circ}30'$ ; refractive index, 1.4911; and boils at  $89^{\circ}$  at 5 mm. It yields an oxime melting at  $87^{\circ}$  to  $88^{\circ}$ , and a semicarbazone melting at  $204^{\circ}$  to  $205^{\circ}$ .

**PHENOLS, DETERMINATION OF.**—The general method for the determination of phenols in essential oils is their absorption by means of a solution of caustic alkali, and measuring the unabsorbed portion of the oil. As in all absorption processes, the results are only approximate, as errors are introduced by

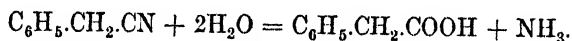
## PERFUMERY

(g) the solubility of the non-phenols in the alkaline solution of the phenol, and (b) the retention of phenols in the non-phenolic residue.

It is difficult to lay down exact conditions which will give the best results for *all* oils, as different oils may require different conditions for obtaining the most accurate results; but in general, sufficiently accurate results may be obtained by repeatedly shaking 10 c.c. of the oil in a Hirschsohn flask, with about 100 c.c. of 5 per cent. solution of caustic soda, for about fifteen minutes on a water bath, and then filling the flask with the solution and allowing it to stand for at least twelve hours before the unabsorbed residue is read off in the neck of the flask. (For critical experiments on these conditions, see *P. & E. O. R.*, 1921, 384; 1923, 138.)

For special methods for determining particular phenols, etc., see "The Chemistry of Essential Oils, etc." (E. J. Parry; vol. ii., p. 348).

**PHENYL ACETIC ACID.**—This acid, of the formula  $C_6H_5.CH_2.COOH$ , is a crystalline body occurring in oil of neroli, and probably in otto of rose, melting at  $76^\circ$  to  $76.5^\circ$ . It has a sweet odour recalling that of honey, and is very useful in the modification of many floral odours. It is prepared by the hydrolysis of benzyl cyanide, either by acid or alkaline solutions, thus:—



Details of the process will be found under "Phenyl-ethyl Alcohol."

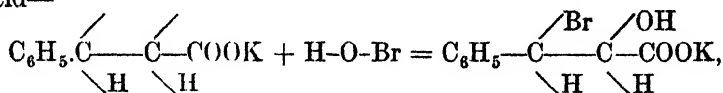
The acid itself is of considerable value in perfumery, but it also forms a number of esters which are of extreme value in the preparation of floral odours. (See Isobutyl, Butyl, Methyl, and Ethyl "Phenylacetates.")

**PHENYL-ACETIC ALDEHYDE.**—This aldehyde, of the formula  $C_6H_5.CH_2CHO$ , is one of the very important modern synthetic perfumes. It is also known as *ortho*-toluic aldehyde. It is the principal basis of artificial hyacinth and the allied flower perfumes. It is a colourless oil, liable to polymerise, and therefore best preserved in the form of a 5 or 10 per cent. solution in alcohol. It can be made by various methods, that of Erdmann being one of the principal.

The potassium or sodium salt of cinnamic acid,  $C_6H_5.CH=CH.COOK$ , is treated with an alkaline solution of bromine, and

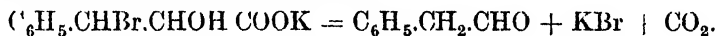
## P E R F U M E R Y

then there is added a weak acid, such as oxalic or boric; this causes the unsaturated structure to combine with hypobromous acid—



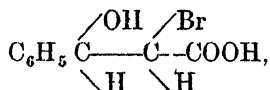
giving the potassium salt of phenyl-bromo-lactic acid.

On steam distillation this compound decomposes with the evolution of carbon dioxide and the production of potassium bromide and phenyl acetaldehyde—



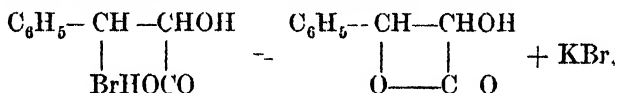
The yield should be about 60 per cent on the weight of cinnamic acid used.

As a matter of fact this reaction is not quite so simple as has been stated, and notable quantities of bromo styrol,  $\text{C}_6\text{H}_5\text{.CH} = \text{CHBr}$ , are always obtained at the same time. The hypobromous acid can naturally add itself on in another way, to give



and this also decomposes, yielding carbon dioxide, water, and bromo styrol.

Some workers have given a different interpretation to this reaction, for example, the salt of phenyl-bromo-lactic acid,  $\text{C}_6\text{H}_5\text{.CHBr.CHOH.COOK}$ , is considered to form a lactone—



the beta lactone of phenyl-alpha-oxy-propionic acid, and this lactone loses carbon dioxide, being converted into phenyl acetaldehyde.

It is interesting to know that this lactone has actually been isolated, and melts at 83°-84°.

The method of carrying out this process is as follows. Cinnamic acid (150 parts) is dissolved in 150 parts of water and 108 parts of 50 per cent. solution of caustic potash. The mixture is evaporated to one-third its volume and cooled. There are then added 1,500 parts of ice and 200 parts of crystallised boric acid. A solution of hypobromite of soda prepared with 200 parts of 50 per cent. solution of caustic potash free from carbonate and 220 parts of bromine (care being taken to avoid rise in temperature) is then



## P E R F U M E R Y

the benzoyl compound heated with phosphorus pentachloride, when chlorides of the formula  $XCH_2Cl$  are formed. These are directly convertible into the corresponding alcohols. Phenyl-amy! alcohol, so prepared, has a pleasant, lemon-like odour. It boils at  $155^\circ$  at 20 mm.

**PHENYL-BUTYL ALCOHOL.**—See “Phenyl-amy! Alcohol”—This alcohol boils at  $140^\circ$  at 14 mm. It has a rose-like odour.

**PHENYL-ETHYL ALCOHOL.**—This alcohol, of the formula  $C_6H_5CH_2CH_2OH$ , is a natural constituent of otto of rose and oils of neroli, champaca, and geranium. On account of its very high solubility it is dissolved to a very considerable extent in the distillation water, and thus disappears to a very large extent from the essential oils themselves. This fact accounts for the difference in odour, for example, between otto of rose and rose concrete or rose water. The alcohol is today made on a considerable scale synthetically, and is of the greatest value in the manufacture of artificial otto of rose and in the modification of many floral perfumes. Phenyl ethyl alcohol requires considerable skill in manufacture, and unless very pure, does not keep well. The greatest care should be exercised in the purchase of this substance, as the commercial article varies enormously in quality. When pure it has a fresh sweet rose-like odour. Its physical characters are as follows —

|                  |                                     |
|------------------|-------------------------------------|
| Specific gravity | 1.024                               |
| Refractive index | 1.5321                              |
| Boiling point    | $220^\circ$ – $222^\circ$ at 740 mm |

It yields a diphenyl methane melting at  $99^\circ$  to  $100^\circ$ , a phthalic acid ester melting at  $158^\circ$  to  $159^\circ$ , and a phenyl methane melting at  $80^\circ$ .

It is exceedingly soluble in water, 1 volume dissolving in 60 of water. It is also very soluble in dilute alcohol—in 18 volumes of 30 per cent. and in 2 volumes of 50 per cent. alcohol.

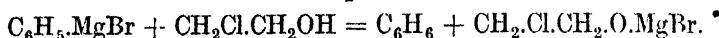
There are two principal methods for the production of this alcohol which may be described. The former of these is the magnesium condensation of Grignard (*Ann. Chem. et Phys.*, 1910, 10, 23). The magnesium compound of brombenzene is condensed with glycol monochloride. The reaction takes place as follows —

One and a half molecular equivalents of brombenzene are allowed to react with one and a half equivalents of magnesium,

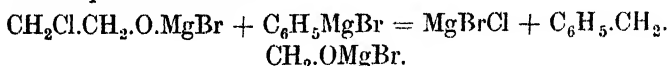


## P E R F U M E R Y

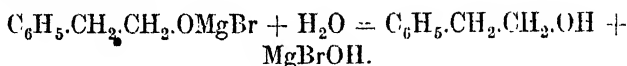
and then 0.5 of a molecular equivalent of the monochloride added. The reaction is brisk and takes place as follows :—



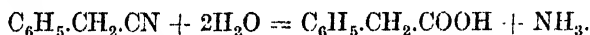
The reaction mixture is cooled and transferred to a distillation flask, heated on a water bath, and finally distilled. The reaction now takes place as follows :—



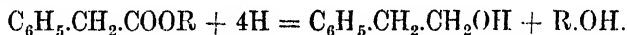
The product of distillation is poured into ice water, when the alcohol is formed—



The second principal method for the preparation of this alcohol is by a reduction process. Benzyl chloride is allowed to react with sodium cyanide in the presence of alcohol. The resulting benzyl cyanide is hydrolysed by a solution of caustic soda (or by dilute sulphuric acid), which results in the formation of phenyl-acetic acid—



The phenyl-acetic acid is then esterified with amyl, ethyl, or methyl alcohol, and the ester formed is reduced with sodium and alcohol—



The following detailed account of its manufacture is due to Lewinsohn (*P. & E. O. R.*, 1923, 336) :—

Five operations are involved—

- (1) Preparation of benzyl cyanide.
- (2) Hydrolysis to phenylacetic acid.
- (3) Esterification of the acid.
- (4) Preparation of 100 per cent. absolute alcohol.
- (5) Reduction of phenylacetic ester.

(1) *Benzyl Cyanide*.—Six kilograms of potassium cyanide are dissolved in water in an enamelled stirring vessel fitted with reflux condenser. There is then added slowly a solution of 10 kg. of benzyl chloride in an equal weight of alcohol. When all has been added, the mixture is heated for three to four hours at the boil. The liquid separates into two layers; the upper one, reddish-brown, contains the benzyl cyanide; the lower aqueous layer the alcohol and potassium chloride (which is precipitated as a crust on the walls of the vessel on cooling).

## PERFUMERY

The brown oily layer is washed several times with water and then distilled at ordinary pressure. Traces of alcohol first come over, and the temperature then rises quickly to  $195^{\circ}$ . The residual liquor is now cooled somewhat and the benzyl cyanide distilled off *in vacuo* without fractionation. The crude benzyl cyanide so obtained is used for the next operation.

(2) *Phenylacetic Acid*.—In a silica basin of about 35 cm. diameter a mixture of 2.5 kg. of benzyl cyanide and 7.5 kg. of 70 per cent. sulphuric acid is warmed until a few bubbles of gas appear. The heating is at once stopped, since a very vigorous reaction now ensues. As the vapours evolved are injurious to health, the basin is covered, when the reaction begins, with a sliding cover, from which the vapours can be led into water. As soon as the reaction ceases, the product is poured upon crushed ice in a large earthenware vessel. Crude phenylacetic acid, contaminated on the surface with phenylacetamide, is precipitated on cooling. In order to remove the amide, the acid is dissolved in lukewarm dilute soda solution. The amide remains undissolved, and can be filtered off, while the phenylacetic acid goes into solution as sodium salt, and is reprecipitated in a sufficiently pure state by the addition of dilute mineral acid. After drying it is ready for esterification.

Phenylacetic acid, as well as its ester, is used for the preparation of honey aroma. For this purpose a further purification is necessary. The acid is dissolved in five times its weight of boiling water, filtered hot, and allowed to cool. Phenylacetic acid separates out in an absolutely pure state in the form of flakes with a mother-of-pearl lustre. After filtering and drying, it possesses a pleasant honey scent.

(3) *Phenylacetic Ethyl Ester*.—The usual method of esterification is employed. A mixture of 10 kg. of phenylacetic acid, 10 kg. of 96 per cent. ethyl alcohol, and 0.5 kg. of concentrated sulphuric acid ( $66^{\circ}$  Bé.) is boiled for three hours in an enamelled vessel fitted with good reflux condenser. Two-thirds of the alcohol is then distilled off, and the residue poured into cold water. The oily layer of phenylacetic ester is separated, washed with water, sodium carbonate solution, and again with water, and finally distilled in vacuum. The pure ester boils at  $91^{\circ}$  to  $92^{\circ}$  at 3 mm.

(4) *Preparation of 100 per cent Alcohol*.—We come now to the most important operation of the whole process, namely, the preparation of a truly absolute alcohol. The so-called absolute alcohol of commerce is never 100 per cent., but at most 99.5 per

cent. Although the amount of water present is so small, it is sufficient, in the presence of the sodium, to hydrolyse the phenylacetic ester before reduction takes place. It is necessary, therefore, to remove this  $\frac{1}{2}$  per cent. of water from the alcohol. Without detailing the rather complicated arrangements by which the transference of the alcohol from vessel to vessel without coming into contact with the air is achieved, we shall limit ourselves to a description of the preparation.

Thirty kilograms of commercial "absolute alcohol" are refluxed for one hour in an iron vessel with 0.300 kg. of calcium turnings. At the end of this time 3 kg. (the "first runnings") are very carefully distilled off. The next 24 kg. form the "main distillate," and there remain about 3 kg. of "last runnings," which are also distilled, and can be added to the next batch. The "main distillate" is run into a dry container, from which it is returned to the distilling vessel after the latter has been emptied of the lime sludge and thoroughly cleaned. Here it is treated with a further 0.240 kg. of calcium turnings and the distillation repeated. After 2.5 kg. of "first runnings" have been collected, the "main distillate," this time 18.5 kg., is run directly into the reduction vessel, in which the air has previously been displaced by hydrogen. The "last runnings," as before, are added to the next batch. The specific gravity of the alcohol, which is measured by means of a special arrangement during the distillation, without bringing the alcohol into contact with the air, must fall from 0.7975 at 15° to 0.7944 at 15° before the alcohol is allowed to enter the reduction vessel.

(5) *Reduction of Phenylacetic Ester.*—The reduction is carried out in a capacious iron vessel with a good reflux condenser, and fitted with a cover in which is a hole which can be quickly opened or closed by means of a suitable arrangement. To the 18.5 kg. of special absolute alcohol collected in this vessel are added 3 kg. of phenylacetic ester, and then 0.20 kg. of calcium turnings. The vessel is now heated to 135° by passing superheated steam through the jacket. At this temperature is begun the addition of 3.5 kg. of metallic sodium. This is added in lots of 500 grams, the opening being rapidly opened and as rapidly closed for each addition. The heating is then continued until there is no further evolution of hydrogen and all the sodium is dissolved.

In order to destroy the sodium ethylate and phenylethylate, 5 kg. of 50 per cent. alcohol are now slowly run in, the water so supplied being sufficient to convert all the sodium present into

**PHENYL-HEXYL ALCOHOL.**—See “Phenyl-amyl Alcohol.”—This alcohol boils at 160° to 161° at 13 mm. It has an odour recalling lemon and roses.

**PHENYL-PROPYL ACETATE.**—This ester is prepared by the acetylation of phenyl-propyl alcohol, and is an ester of sweet rose odour. It is probably present in cassia oil.

**PHENYL - PROPYL ALCOHOL.**—This homologue of phenyl-ethyl alcohol, of the formula  $C_6H_5.CH_2.CH_2.CH_2.OH$ , is also known as hydrocinnamyl alcohol. It is present in storax as its cinnamic acid ester, and in cassia oil in the form of its acetic ester. It may be prepared artificially by the reduction of cinnamyl alcohol with sodium amalgam and water, or by the reduction of the acetic ester of either cinnamyl or benzyl alcohol with sodium and absolute alcohol. It has a specific gravity 1.007, refractive index 1.5260, and boils at 235°. It forms a phenyl-urethane melting at 47° to 48°. It is a colourless, viscous oil having a sweet odour of hyacinth and mignonette. It is used in the preparation of artificial hyacinth, jonquil, narcissus, mignonette, and similar odours. There are several isomers of this alcohol which have fragrant floral odours, but which are not, so far, commercial articles. These are: benzyl-methyl carbinol,  $C_6H_5.CH_2.CH(OH)(CH_3)$ , boiling at 215°; phenyl-ethyl carbinol,  $C_6H_5.CH(OH)(CH_2.CH_3)$ , boiling at 221°; and benzyl-dimethyl carbinol,  $(C_6H_5.C(OH)(CH_3)_2)$ , melting at 21° and boiling at 225°.

**PHENYL-PROPYL ALDEHYDE.**—This aldehyde is stated to be present in oil of cinnamon bark. It is a colourless oil, of the formula  $C_6H_5.CH_2.CH_2.CHO$ , having an odour of hyacinth, and is useful in the preparation of artificial hyacinth or lilac perfumes. It is more stable than phenyl-acetic aldehyde, and is prepared by the same general methods as that body.

**PHENYL-PROPYL CINNAMATE.**—This ester occurs naturally in storax, and has a heavy, balsamic perfume. It is a very useful fixative.

**PHEROSPHERA FITZGERALDI, OIL OF.**—According to Baker and Smith (“The Pines of Australia,” 412), the leaves of this plant, which grows freely in New South Wales, yield an essential oil which consists mainly of terpenes, but also contains a small quantity of esters.

**PHLORACETOPHENONE - DIMETHYL ETHER.**—This substance is an ether, of the formula  $C_{10}H_{12}O_4$ . It is present in the oil of *Blumea balsamifera*. It is a colourless crystalline

## P E R F U M E R Y

compound melting at  $82^{\circ}$  to  $83^{\circ}$ , and yields an oxime melting at  $108^{\circ}$  to  $110^{\circ}$ .

**PHOBEROS COCHINCHINENSIS.**—*Roure-Bertrund Fils* (*Bulletin*, April, 1914, 7) have examined the essential oil distilled from the leaves and stalks of this tree, belonging to the natural order *Flacourtiaceæ*, which is found growing wild in Annam. The oil has a distinct orange odour, and has the following characters :—

|                               |           |                  |
|-------------------------------|-----------|------------------|
| Specific gravity              | . . . . . | 0.9042           |
| Optical rotation              | . . . . . | + $3^{\circ} 2'$ |
| Acid value                    | . . . . . | 2.5              |
| Ester value                   | . . . . . | 51.1             |
| Ester value after acetylation | . . . . . | 127.9            |

**PHYLLANTHUS COCHINCHINENSIS.**—See “Bruyère d’Annam.”

**PILOCARPUS LEAF OIL.**—The leaves of *Pilocarpus Jaborandi* yield about 5 per cent. of essential oil which contains the odorous ketone methyl-nonyl ketone. It has a specific gravity 0.865 to 0.895, and is slightly dextrorotatory.

**PIMENTO.**—*Vide* “Allspice.”

**PINE-NEEDLE OILS.**—The term “Pine-needle oil” is a somewhat elastic one, as it includes, from a scientific point of view, an enormous number of essential oils distilled from the leaves of various species of *Pinus*, *Larix*, and *Abies*. From the perfumer’s point of view the only oils of any value are those containing a substantial percentage of esters (bornyl acetate). Of these the most important is the oil of *Abies Sibirica*, which is produced principally in north-east Russia, especially in the Wjatka district. This oil has a very fragrant odour of the “pine forest,” and is used to a considerable extent in cheap perfumery, especially in the manufacture of bath crystals, theatre sprays, and similar popular productions. It has the following characters :—

|                           |           |                           |
|---------------------------|-----------|---------------------------|
| Specific gravity          | . . . . . | 0.900–0.928               |
| Optical rotation          | . . . . . | – $30'$ to – $45^{\circ}$ |
| Refractive index          | . . . . . | 1.4700–1.4740             |
| Esters, as bornyl acetate | . . . . . | 29–45 per cent.           |

The oil contains terpenes, a sesquiterpene, bornyl acetate, and small quantities of terpinyl esters.

The leaves of the Douglas fir yield an aromatic essential oil,

## P E R F U M E R Y

which has been examined by C. T. Bennett. The oil has also been examined by Brandel and Sweet, and by Schorger, but as there are two trees known by this name, and the botanical source of the material examined by Bennett appears to be authentic, his results may be accepted with confidence. *Pseudotsuga taxifolia* is the so-called Douglas fir growing in Oregon, whilst the blue Douglas fir of Colorado is *Pinus glauca*. Bennett has examined both oils, distilled from material grown in England, and reported on them as follows:—

*Oil from Leaves of the Oregon Douglas Fir.*—(1) Fifty pounds of leaves of young trees growing at Avondale, sent in August, 1919. When distilled, less than 0.01 per cent. of an oil with a very aromatic odour was obtained—a quantity too small for examination.

(2) Fifty pounds of leaves of old trees growing at Buckhold, Berks, sent in November, 1919, when distilled yielded 0.11 per cent. of oil having the following characters:—

|                                    |                |
|------------------------------------|----------------|
| Specific gravity . . . . .         | 0.876          |
| Optical rotation . . . . .         | — 7'           |
| Refractive index . . . . .         | 1.4835         |
| Esters as bornyl acetate . . . . . | 12.4 per cent. |

The ester content is much lower than that of the Colorado Douglas fir oil, but the odour is more fragrant. The oil contains dipentene or limonene, but if pinene is present, the quantity is very small, as practically nothing distils below 175°.

(3) A few days later another 50 lb. of leaves from the Oregon Douglas fir from Buckhold were distilled, and enough oil was then available for further investigation. On fractionating the oil, an appreciable quantity of geraniol was separated, and this appears to be the chief odorous constituent. The proportion of total alcohols by acetylation calculated as geraniol is 31.5 per cent. The presence of bornyl acetate somewhat masks the odour of geraniol in the original oil. There is also a small trace of citral, but the proportion is too small for determination. Geraniol occurs in the oils of some species of *Callitris* in Australia, but has, apparently, not been recorded as a constituent of the oils distilled from other conifers. Geraniol is the chief constituent of Indian palmarosa oil obtained from the fragrant grass *Cymbopogon Martini* (*Andropogon Schænanthus*), and occurs in citronella oil, otto of roses, lemon oil, etc.

*Oil from the Leaves of the Colorado Douglas Fir.*—Fifty pounds of leaves of moderate sized trees, growing at East Liss, Hants, sent

## P E R F U M E R Y

in October, 1919, yielded on distillation 0.31 per cent. of oil having the following characters :—

|                                    |                |
|------------------------------------|----------------|
| Specific gravity . . . . .         | 0.905          |
| Optical rotation . . . . .         | — 46°          |
| Refractive index . . . . .         | 1.4717         |
| Esters as bornyl acetate . . . . . | 34.5 per cent. |

The terpenes consist principally of pinene. The odour is chiefly due to the bornyl acetate present. It would appear from these analyses that the strong odour of Colorado Douglas fir, which is like that of turpentine mixed with camphor, is due to the large percentage of pinene and bornyl acetate. In the Oregon Douglas fir pinene is not present, and the bornyl acetate is much less in percentage. The peculiar fragrance is chiefly due to the presence of the highly odoriferous substance geraniol, slightly modified by the small amount of bornyl acetate present.

For numerous other pine-needle oils, mostly containing only a small percentage of bornyl acetate, reference may be made to the "Chemistry of Essential Oils and Artificial Perfumes," 4th ed., vol. i. (Scott, Greenwood & Co.).

**PINOCARVEOL.**—This substance is an alcohol of the formula  $C_{10}H_{16}O$ . It exists in oil of *Eucalyptus globulus*, and can be prepared artificially by treating pinylamine nitrate with sodium nitrite. The yellowish oil which separates is distilled with steam, and basic compounds are removed from the distillate by shaking with a solution of oxalic acid. The oil is then redistilled with steam, and the pure alcohol results. It is an aromatic oil, with an odour somewhat resembling pine oil, and having the following characters :—

|                             |           |
|-----------------------------|-----------|
| Boiling point . . . . .     | 215°–218° |
| Specific gravity . . . . .  | 0.978     |
| Refractive index . . . . .  | 1.4963    |
| Specific rotation . . . . . | — 52° 45' |

It forms two isomeric phenyl-urethanes melting at 82° to 84° and 94° to 95° respectively.

**PINOGLYCYL ESTERS.**—The alcohol pinoglycol  $C_{10}H_{16}O(OH)_2$  can be esterified, and yields esters with a marked fruity odour. Of these, the acetate  $C_{10}H_{16}O(C_2H_3O_2)_2$ , melting at 97° to 98°, and the propionate  $C_{10}H_{16}O(C_3H_5O_2)_2$  are the best known.

**PINENOL.**—According to Genvresse (*Comptes Rendus*, 130, 918), pinenol is a compound of the formula  $C_{10}H_{16}OH$ , which

## P E R F U M E R Y

results from the action of nitrous fumes on ice-cold pinene. It has the following characters:—

|                   |                 |
|-------------------|-----------------|
| Boiling point     | 225° at 740 mm. |
| Specific gravity  | 0.9952 at 0°    |
| Refractive index  | 1.4970          |
| Specific rotation | — 14.66°        |

It forms an acetic ester  $C_{10}H_{15} \cdot OOC \cdot CH_3$  which boils at 150° at a pressure of 40 mm. This ester, pinenyl acetate, has a marked odour of lavender.

**PINENYL ACETATE.**—See “Pinenol.”

**PIPERITONE.**—This highly interesting ketone has recently been the subject of a good deal of research, as, apart from its intrinsic interest, it presents considerable economic possibility in reference to the artificial preparation of both thymol and menthol. According to Baker and Smith (“The Eucalypts and their Essential Oils,” 2nd ed., p. 390) this unsaturated aromatic ketone is more generally distributed in the oils of eucalypts growing in the eastern and south-eastern portion of Australia and in Tasmania, where the members of the whole group are known vernacularly as “Peppermints.”

This peppermint odour was noticed by the first white settlers in Australia in 1788, and oil was distilled by them at that time from the leaves of *Eucalyptus piperita*, a tree somewhat extensively distributed around Sydney, the coastal ranges, and coastal districts of New South Wales and Victoria. It is thus worthy of notice that both the vernacular name “peppermint” and the scientific name *Eucalyptus piperita* were given to this tree on account of the presence of this peppermint constituent in the oil; in fact, chemical constituents were often a guiding factor in the early naming of eucalypts.

On the mountain ranges in New South Wales and Victoria, as well as in Tasmania, the members of the “peppermint” group of eucalypts form a large proportion of the natural vegetation, and are distributed over hundreds of square miles of country.

It is now recognised that all the principal constituents found in eucalyptus oils increase in amount through a range of species until a maximum is reached in one or more of them. Piperitone follows this rule, and *Eucalyptus dives*, a “broad-leaved peppermint,” appears to be the species in which it reaches a maximum content. This eucalypt is one of the most plentiful of all the members of the “peppermint” group, and also gives a good yield of oil, averaging from 3 to 4 per cent., according to the time of year, the



care taken in collecting, and on the duration of the primary distillation, and if this be somewhat extended, say from six to eight hours, the oil will often contain as much as from 40 to 50 per cent. of piperitone. It is thus evident that this ketone could be produced in great quantity, and at a cheap rate. The remainder of the oil of *E. dives* consists largely of phellandrene, and is employed in the mining industry for flotation work, as well as for other economic purposes.

Piperitone is the only ketone found in eucalyptus oil, and appears to occur only in the oils of species occupying the more recent end of the genus, and is not found in the oil of any member of the groups occupying the anterior position in the evolutionary sequence of the genus.

Although piperitone is usually found occurring with phellandrene, yet, in the case of *E. apiculata*, this terpene was not detected; and altogether the oil of this species was of such a character as not to be readily placed in any of the well-defined groups.

In the oils of most species piperitone is found associated with the corresponding levorotatory secondary alcohol piperitol, and Baker and Smith have isolated this alcohol from the oil of *E. radiata*, where it occurs as a well-defined constituent.

Under natural conditions piperitone is levorotatory, but readily forms the racemic modification when heated above its boiling point, in the process of separation by direct distillation of the original oil. This alteration appears to be brought about largely by the influence of the acid from the esters, under the conditions stated, because the pure ketone undergoes little alteration when distilled directly, but if geranyl-acetate be first added the alteration in rotation is considerable.

It was due to this tendency to racemisation that in the original paper in which the ketone was described, it was shown to be inactive, as it had been first obtained in the crude condition by direct distillation of the original oil. If, however, the first separation be carried out under greatly reduced pressure, the levorotatory form can be separated and prepared in a pure condition by the aid of sodium bisulphite. This compound of piperitone is very soluble in aqueous solution, but after the lapse of several days the saturated liquid forms a crystalline mass from which pure piperitone can be recovered, although there is often a considerable reduction in rotation. Piperitone can also be removed by the aid of the neutral sodium sulphite.

## PERFUMERY

Piperitone has considerable prospective economic value, in that it forms thymol by treatment with ferric chloride, inactive menthone by reduction, when a nickel catalyst is employed, and inactive menthol by the reduction of the menthone with sodium in an aqueous ether solution. (These reactions were first described by H. G. Smith and A. R. Penfold in a paper read before the Royal Society of New South Wales June, 1920.)

As piperitone can be obtained in very large quantity, the production of one or more of these substances from this ketone on a manufacturing scale seems most promising, and should be profitable when the best conditions for commercial purposes shall have been worked out.

Piperitone being an unsaturated ketone with one double bond, it follows, from the above, that it must be a menthenone with the carbonyl group in the 3 position. This is proved by the formation of thymol and menthone. When piperitone is oxidised in the cold with potassium permanganate in alkaline solution, isobutyric acid is one of the products of oxidation, and it does not seem possible to entirely prevent the formation of this acid at any stage of the process even when the temperature is kept down by the addition of ice and the theoretical amount of permanganate employed. From the ready formation of isobutyric acid it might be supposed that the double bond was in the 4 position, but so far the corresponding  $\beta$  methylglutaric acid has not been prepared.

Wallach and Meister (*Annalen* 1908 **362**, 261) have, however, shown that  $\Delta$  4 menthenone 3 boiled at 212 to 213°, but Auwers (*Berichte* 1908 **41**, 1801 and 1909 **42**, 2405) doubts the correctness of this statement, although Wallach (*Chem. Zentr.*, 1912 **11**, 922-923) confirmed his original determination. The question whether piperitone is  $\Delta$ -4 menthenone 3 or  $\Delta$  1 menthenone 3, remains at present unsettled, and the formation of menthone and menthol does not assist in deciding the position of the double bond.

Piperitone has a peppermint odour and taste resembling pulegone very closely in these respects. It is colourless when pure, but becomes yellowish with age. It reduces an alkaline solution of silver nitrate, and reproduces the red colour with Schiff's reagent.

Two methods are available for the separation of piperitone for works practice, both of which give good results, viz. —

- (1) (a) The crude oil is subjected to distillation in a pot still, and

## PERFUMERY

the portion boiling below  $220^{\circ}$  at atmospheric pressure (principally phellandrene) or  $100^{\circ}$  at 10 mm. is collected separately.

The piperitone which has a boiling point of  $229^{\circ}$  to  $230^{\circ}$  at 760 mm. (or  $106^{\circ}$  to  $108^{\circ}$  at 10 mm.) will be obtained in the second fraction distilling between  $221^{\circ}$  to  $236^{\circ}$  at atmospheric pressure or  $100^{\circ}$  to  $112^{\circ}$  at 10 mm.

If reduced pressure is not available, and as a temperature of  $221^{\circ}$  to  $236^{\circ}$  is rather high for pot-still distillation, decomposition being rather difficult to avoid, the following alternative procedure may be followed, viz. :—

(b) After removal of the phellandrene fraction, the residue may be subjected to fractional steam distillation, the piperitone thus becoming concentrated in an intermediate fraction, the process being controlled by means of the refractometer.

(2) Instead of direct distillation, provided the oil is rich in piperitone (not less than 48 per cent.), the phellandrene can be removed by means of a rapid current of steam. After its removal, the ketone can be obtained from the residue by either the (a) or (b) procedure of method No. (1).

Commercial piperitone thus prepared contains usually about 90 per cent. actual ketone, and is sufficiently pure for conversion into thymol.

If the oil has been subjected to distillation at atmospheric pressure, the ketone is very slightly active, usually about  $-0.4^{\circ}$  to  $-1^{\circ}$ , but if separated by means of fractional steam distillation throughout, the optical activity is about  $-43^{\circ}$  to  $-46^{\circ}$ .

Should the ketone be required of a greater degree of purity, say, about 95 per cent., it can be readily obtained by fractional distillation. To prepare it of about 99 per cent. purity, use is made of its property, in common with many other ketones, of reacting with either sodium bisulphite or sodium sulphite solutions.

Two laboratory methods of preparation are available :—

(1) Four hundred cubic centimetres 30 per cent. sodium bisulphite solution (pure), 280 c.c. 90 per cent. piperitone, 80 c.c. special methylated spirit (5 per cent. wood naphtha) are mixed in the order given and shaken, at constant intervals only, for about three to seven days until combination is practically complete. The aqueous solution is separated at once (if allowed to stand, the bisulphite compound crystallises out) from the unabsorbed oil, and on treatment with a 20 to 25 per cent. solution of caustic soda the ketone is liberated, which, after washing to

## P E R F U M E R Y

free it from alkali, may be purified by either steam or direct distillation

• (2) Three hundred cubic centimetres, 90 per cent ketone are shaken with a litre of 35 per cent solution of crystallised sodium sulphite, using phenolphthalein as an indicator the liberated alkali being neutralised from time to time with 1·3 sulphuric acid solution. When the reaction is completed and after removal of unabsorbed oil, the ketone is regenerated by addition of 20 per cent caustic soda solution

Piperitone has the following characters —

|                        |   |
|------------------------|---|
| Boiling point          | 229–230° at 760 mm<br>(uncorrected)<br>235° (corrected)<br>106–108 at 10 mm |
| Specific gravity       | 0·9348 at 20<br>0·9393 at 15  |
| Optical rotation       | Variable 0·4 to —50·2   |
| Refractive index       | 1·4837 at 20  |
| Oxime                  | Melting point 117–118   |
| Oximino oxime          | 169–170   |
| Semicarbazone $\alpha$ | 225–226   |
| $\beta$                | 175–176   |
| $\beta$ isomeric       | 188–189   |
| Benzylidene derivative | 61  |
| Bis nitroso derivative | 96°–97°   |

The following are the reduction and oxidation reactions —

*Products of Reduction* With sodium in aqueous ether menthol, together with a pinacone and resinous products

With sodium amalgam in alcoholic solution—a pinacone (dimolecular ketone) melting point 142 to 149

With hydrogen in presence of nickel—menthone

*Products of Oxidation*—With ferric chloride in acetic acid solution thymol

With potassium permanganate solutions—diisphenol,  $\alpha$  hydroxy  $\alpha$  methyl  $\alpha$  isopropyl adipic acid  $\alpha$  isopropyl  $\gamma$  acetyl butyric acid and  $\alpha$  isopropyl glutaric acid

It possesses the structure of a  $\Delta'$  menthenone 3

Penfold (*Bulletin* No 1 1921 Technological Education Branch, Technological Museum Sydney) gives the following methods for the detection and determination of piperitone

The formation of the bimolecular ketone, ( $C_{20}H_{34}O_2$ ), by the procedure about to be described, enables piperitone to be detected in 1 c.c. of oil containing but 10 per cent of ketone. One cubic centimetre of *E. dives* oil is mixed with 1 c.c. alcohol (special

## PERFUMERY

methyiated spirit) and 4 c c ether, and 1 gram 3 per cent sodium amalgam added. If piperitone is present, a reddish brown coloration is immediately produced, and at the end of about ten minutes a copious white crystalline precipitate separates. In the absence of ether, the reaction requires several hours' standing for completion. If it is desired to isolate this pinacone, it can be filtered, washed with ether dried, crystallised from absolute alcohol (boiling), and its melting point determined. It melts somewhat indefinitely, and variably between  $142^{\circ}$  and  $149^{\circ}$ .

Penfold has been successful in separating this body, by fractional precipitation from chloroform solution into two bodies, melting at  $135^{\circ}$  to  $136^{\circ}$  and  $166^{\circ}$  to  $167^{\circ}$ .

The Burgess method for the estimation of aldehydes and ketones gives excellent results with the oil of *E. dives*, and has been in use by Penfold for the past four years. Five cubic centimetres of the oil are pipetted into a cassia flask of about 150 c c capacity with a neck graduated, 5 c c. in one tenths, a solution of crystallised sodium sulphite added (made by dissolving 350 grams of the crystallised salt plus 1,000 c c water together) to fill about two thirds of the flask,  $\frac{1}{2}$  c c phenolphthalein indicator added, and the flask and contents heated in a vigorously boiling water bath with constant agitation of contents. The liberated alkali is neutralised from time to time by means of 10 per cent acetic acid solution until reaction is complete. The volume is gradually made up with the sulphite solution and finally the unabsorbed oil is forced up into the neck of the flask and when cold the volume is read off. The difference in volume between the unabsorbed oil and 5 c c (original volume taken) represents the amount of piperitone present in that volume, which on multiplication by 20 gives the percentage present. Over fifty determinations made on oils distilled right out have given results averaging between 40 and 50 per cent ketone.

Gavaudan (*P & E O R*, 1921, 80) drew attention to the similarity of piperitone with certain other ketones (all of which were discovered later than piperitone), and considered these bodies to be all identical. Penfold (*P & E O R*, 1922, 19) agrees with these suggestions, namely, that piperitone is identical with the following compounds —

(1)  $\Delta'$  Menthenone-3 prepared synthetically by Wallach (*Annalen*, 1908, 362, 271)

(2) The ketone found occurring in Japanese peppermint oil, identical with (1) (*Schummel & Co, Report*, October, 1910, 97).

## P E R F U M E R Y

(3) The ketone found in camphor oil, identical with (1) (Gilde-meister and Hoffmann, 2nd German ed., p. 482).

(4)  $\Delta'$ -Menthenone-3 found in the oil of *Cymbopogon sennaarensis* (Roberts, *Jour. Chem. Soc.*, 1915, **107**, 1465).

The name piperitone takes priority for this ketone,  $\Delta'$ -menthenone-3, as it was first discovered by H. G. Smith, F.C.S., in eucalyptus oils in the year 1900 (*Jour. Roy. Soc. N.S.W.*, 1900, vol. xxxiv., p. 136).

Simonsen has also shown (*Jour. Chem. Soc.*, 1921, **78**, 1644) that the essential oil of *Andropogon inarancusa*, an Indian grass, contains about 80 per cent. of a ketone which is the dextrorotatory form of piperitone.

For the exact constitution of piperitone, see *Jour. Chem. Soc.*, 1924, 129.

M. D.

**PIPERONAL.**—See “Heliotropin.”

**PISTACIA OIL.**—Mastic resin, from *Pistacia lentiscus* (natural order *Anacardiaceæ*), a tree growing in southern Europe, north Africa and the Levant, yields about 1 to 2.5 per cent. of essential oil, having a characteristic aromatic odour. The only constituents identified are terpenes, but the oil is a useful fixative, so probably contains some oxygenated constituents of high molecular weight. It has a specific gravity, 0.850 to 0.905; optical rotation,  $\pm 22$  to  $\pm 35^\circ$ ; and refractive index, 1.4680 to 1.4760.

**PLUMIERA.**—See also “Frangipani.” Certain species of *Plumiera*, which belongs to the natural order *Apocynaceæ*, are the plants known as frangipani. *Plumiera acutifolia*, *P. alba*, and *P. rubra* are the best known species.

**PNEUMUS BOLDO OIL.**—The dried leaves of *Pneumus boldo* yield a small amount of an essential oil of specific gravity from 0.910 to 0.960; optical activity,  $-2^\circ$  to  $+2^\circ$ ; and refractive index, 1.4793. According to Schimmel & Co. (*Bericht*, April, 1888, 43) the oil contains cymene, cineol, and ascaridol,  $C_{10}H_{16}O_2$ . It has an odour resembling that of wormseed.

**POLIANTHES TUBEROSA.**—This plant, commonly known as the tuberose, is a bulbous plant belonging to the natural order *Amaryllidaceæ*. It is probably a native of Mexico. The tuberous bulbs are regularly imported into England from Genoa and from North America, and are cultivated under glass for the sake of their powerfully fragrant white flowers. The perfume is most

## P E R F U M E R Y

powerful in the evening when the light has disappeared, but when cultivated with the aid of artificial heat the perfume is not nearly so fine as that developed by the flowers cultivated in the open air in the south of France. It yields a crop which is collected from July to the middle of October. In the Grasse district the bulbs are planted in April about 10 inches apart in rows about 2 feet apart. The land used for cultivation should be deep, rich soil, as the roots penetrate downwards to a considerable depth in search of moisture. If cultivated on dry soil, the plants require much watering and manuring. Each stem will bear ten to twelve flowers, or even more if the plants are really well cultivated. Each flower is picked as it opens. After the middle of October the flowers are only of use for ornamental purposes, as the fragrance developed is not sufficient to make it worth while for the perfumer to extract it. In November the tubers are taken out of the ground, and packed away in dry sand to preserve them from damp and cold. Propagation is effected by offsets, which are freely produced. The plant was produced in the south of Europe centuries ago, and was first cultivated in Britain in the early half of the seventeenth century. It is frequently known as *Hyacinthus tuberosus*. The flowers emit a very delightful fragrance. In the East the Malays call them the "Mistress of the Night," on account of the intensity of their odour after sunset. The natural perfume of the tuberose is extracted by enfleurage in the cold, because, like jasmine flowers, the tuberose flowers continue to evolve perfume whilst in contact with the fat. A certain amount is also extracted by means of volatile solvents, but tuberose absolute is obtained in so small amount that it is one of the most expensive of all the natural flower perfume materials. The essential oil obtained by the distillation of the enfleurage product has been examined by Hesse (*Berichte*, 1903, **36**, 1459), who found it to have the following characters:—

|                  |   |   |   |                      |
|------------------|---|---|---|----------------------|
| Specific gravity | . | . | . | 1.007-1.043          |
| Optical rotation | . | . | . | — 2° 30' to — 3° 45' |
| Acid value       | . | . | . | 22-32.7              |
| Ester value      | . | . | . | 224-243              |

Verley (*Bull. Soc. Chim.*, 1899, iii., **21**, 307) isolated from the oil a body having the formula  $C_{13}H_{20}O$ , which he considered to be a ketone, and to which he gave the name tuberone. The methyl esters of benzoic and anthranilic acids are also present, the latter to the extent of 1.13 per cent. Methyl salicylate has been found

## P E R F U M E R Y

in the enfleurage oil, but not in the petroleum extracted oil. Benzyl alcohol and benzyl benzoate are also present.

Most tuberose perfumes are mainly artificial mixtures, but the best are based on a certain amount of the natural substance. Isobutyl-phenyl-acetate and para-cresyl phenyl-acetate are usually present in artificial mixtures, as well as geraniol, linalol, methyl anthranilate, benzyl acetate and benzyl alcohol.

**POPLAR BUD OIL.**—The young buds of *Populus nigra*, the black poplar (natural order *Salicinea*), yield about 0.3 to 0.6 per cent. of an essential oil of pale yellow colour, and having an odour somewhat recalling that of camomiles. Its constituents are not definitely identified. The oil has a specific gravity about 0.890 to 0.910, optical rotation,  $\pm 1$  to  $+6^\circ$ , and contains a small quantity of esters and free alcohols.

**POPOWIA CAPEA, OIL OF.**—*Roure-Bertrand Fils* (*Bulletin*, October, 1913, 4, 15) have described the essential oil distilled from the leaves of a plant growing in the Ivory Coast Colony, where it is known as *Capé*. E. G. and A. Camus identified the plant as one of the natural order *Anonacea* and named it *Popowia Capea*. The leaves were distilled and the oil separated into a light oil which floated on the surface of the distillation water, and a heavy oil which sank to the bottom. The characters of the mixed or "complete" essential oil were as follows:—

|  |                |
|--|----------------|
| Specific gravity                       | 1.0042         |
| Optical rotation                       | $\pm 77^\circ$ |
| Acid value                             | 2.8            |
| Saponification value                   | 166.1          |
| Saponification value after acetylation | 239.9          |

**PRIMULA OIL.**—The fresh roots of *Primula officinalis* (natural order *Primulacea*) when crushed develop a marked odour, first recalling that of aniseed, later that of methyl or amyl salicylate. The essential oil is not present in the living root as such, but results from the hydrolysis of two glucosides when the roots are crushed. These glucosides have been separated by Goris, Maseré and Vischnac (*Roure-Bertrand Fils*, *Bulletin*, October, 1912, 3.) and named primeverin and primulaverin. The former,  $C_{30}H_{28}O_{11}$ , melts at  $206^\circ$ , and on hydrolysis yields sugars and the methyl ester of  $\beta$ -methoxyresorcylic acid. This is the solid constituent of the essential oil, melting at  $49^\circ$ , and was previously described as primula camphor (*Innalen*, 1877, 185, 222). Primulaverin,  $C_{20}H_{28}O_{13}$ , melts at  $161^\circ$  to  $163^\circ$ , and on



## PERFUMERY

hydrolysis yields sugars and the methyl ester of *m*-methoxy-salicylic acid, which forms the liquid portion of the essential oil. The roots of *Primula vera* yield a practically identical essential oil.

**PROSTANTHERA CINEOLIFERA.**—Baker and Smith have examined this Australian plant belonging to the natural order *Labiatae*. The leaves yielded 0.71 per cent. of essential oil, having a specific gravity 0.9204; and refractive index, 1.4711 at 22°. The oil contains geranyl acetate, pinene, cymene, free geraniol, eucalyptol, a phenol, and an aldehyde, which is probably cuminic aldehyde.

**PRUNUS OILS.**—The leaves of the cherry laurel *Prunus laurocerasus* yield an oil very similar to essential oil of almonds. This contains benzaldehyde and prussic acid, with possibly traces of benzyl alcohol. Its characters are substantially identical with those of almond oil. The bark of *Prunus virginiana*, the so-called "wild cherry," yields about 0.2 per cent. of essential oil of almost exactly similar characters.

**PSEUDO-CARYOPHYLLUS SERICEUS.**—This plant, also known as *Myrtus pseudo-caryophyllus*, one of the *Myrtaceae*, has leaves which have a clove like odour. The essential oil, which is obtained to the extent of 0.7 per cent., has a specific gravity 0.9487, and contains a little eugenol.

**PTYCHOTIS AJOWAN.**—See "Ajowan Seed Oil."

**PURPULUT.**—This is the Malayan plant *Urena lobata* used commonly as an adulterant of patchouli leaves (*q.v.*).

**PYCNANTHEMUM OILS.**—The oil of *Pycnanthemum lanceolatum* (*Kallia lanceolata*) was formerly described as that of *Thymus virginicus*. It is known in the United States as "mountain mint," and the oil has an odour closely resembling that of American pennyroyal oil. It contains carvacrol, pulegone, geraniol, dipentene, and probably thujone. The oil distilled from young plants contains as much carvacrol as, but less ketones than, the oil from matured plants. The oil has been exhaustively examined by E. R. Miller (*Circular No. 2*, April, 1918, Pharm. Expt. Station, Wisconsin University). It is very variable in characters, according to the time and place of collection of the

## P E R F U M E R Y

distillation material. Twenty-five samples gave figures falling within the following limits :—

|                                |                     |
|--------------------------------|---------------------|
| Yield of oil per cent.         | 0.27–0.72           |
| Specific gravity at 25°        | 0.896–0.9465        |
| Optical rotation               | — 5.95° to + 12.25° |
| Refractive index at 18.9°      | 1.4831–1.5013       |
| Phenols per cent.              | 14.5–53             |
| Ketones „                      | 3.0–40              |
| Acid number                    | 0.54–45.17          |
| Ester number                   | 3.64–33.27          |
| Ester number of acetylated oil | 85.8–193.7          |

*Pycnanthemum incanum* (*Kallia incana*) is known in North America as mountain mint or basil. The oil is of reddish-yellow colour and has a powerful aromatic odour. Its specific gravity is about 0.935.

**PYRETHRUM OILS.**—The feverfew, *Matricaria pyrethrum* (*Pyrethrum parthenium*), yields a very small quantity of a powerfully smelling essential oil, rarely exceeding 0.1 to 0.2 per cent. of the weight of the fresh flowering plant. Dessaignes and Chaubard (*Jour. Prakt. Chem.*, 1848, **45**, 45) first discovered the presence of the rarely occurring *lavo-camphor* in this oil. Bornyl esters are present, and possibly borneol. The oil has a specific gravity from 0.900 to 0.960. The leaves of *Pyrethrum indicum* (*Chrysanthemum japonicum*) yield the ki-ku oil of Japan, and the flowers of the allied plant *Chrysanthemum sinense* var. *japonicum* yield 0.8 per cent. of the oil known as riono-kiku oil. This oil has a specific gravity 0.939, optical rotation — 12°, and contains camphene and inactive camphor.

**PYROGALLOL DIMETHYL ETHER.**—This phenolic ether, of the formula  $C_6H_3(OH)(OCH_3)_2$ , is present in the essential oil of an Algerian plant whose botanical source is not yet identified. It is an odorous body melting at 51°, and yields a benzoyl derivative melting at 107° to 108°.

**RAMONA STACHYOIDES.**—This plant, also known as *Salvia mellifera*, is a plant belonging to the natural order *Labiatae*, found in California, and known there as black sage. It yields about 0.75 per cent. of a fragrant essential oil, which has been examined by F. Rabak (*U.S. Dept. of Agriculture, Bureau of Plant*

## P E R F U M E R Y

*Industry, Bulletin*, No 235, p 14), who found it to have the following characters —

|                               |         |
|-------------------------------|---------|
| Specific gravity at 24°       | 0.9144  |
| Optical rotation              | + 30.2° |
| Refractive index at 24°       | 1.4682  |
| Acid value                    | 2       |
| Ester value                   | 2.5     |
| Ester value after acetylation | 27.1    |

The oil was found to contain camphor, cineol, traces of free acetic and formic acids and probably pinene, thujone and borneol. Burke and Seabone (*Jour. Ind. Eng. Chem.*, 1914, **6**, 804) have more recently examined an oil distilled from the leaves and twigs (yield about 0.9 per cent) collected in February. The oil had a specific gravity 0.898, optical rotation + 24.4°, refractive index 1.4720, acid value 2.2 and ester value 1.6. It was found to contain camphor, cineol, pinene, thujone and inactive terpenes. The oil has a pleasant aromatic odour.

**RANDIA.** There are a number of species of this genus of the natural order *Cinchonaceae* which have highly odorous flowers. The plants are closely allied to the gardenias and the flowers of those species which are fragrant have a perfume similar to that of a typical gardenia. *Randia dumetorum*, *R. spinosa*, *R. uliginosa*, *R. longipinna* and several other species are exceedingly fragrant. They are all tropical plants and their perfume is not prepared commercially.

**RASAMALA WOOD OIL.** Schimmel & Co. (Bericht April, 1892-13) have obtained 0.17 per cent of essential oil from the wood of a tree growing in Dutch Indies and their known as *Rasamala*. Its botanical origin is unknown. The oil forms a semi-solid crystalline mass having an odour recalling those of cinnamon and rhubarb. The principal constituent of the oil is a crystalline body melting at 54° to 55°, probably a ketone, which forms an oxime melting at 106° to 107°.

**RAVENSARA.**—There are about fifteen species of *Ravensara*, a genus of the natural order *Myrtaceae*, to be found in Madagascar, all having some part of the plant which is highly aromatic. The plants have not been carefully examined, and a proper investigation is necessary, as some of them possess considerable potential value for perfumery purposes. Such an investigation is particularly desirable, as the majority of the genus are in danger of extinction through deforestation. The most aromatic parts of

most of the plants are the bark and the fruit. The fruit of some of the species are exported under the name noix de ravinzara for use as a condiment, and to a limited extent as a drug. The species to which attention should be directed are *Ravensara perrieri*, *R. crassifolia*, *R. anisata*, and *R. aromatica*. The leaves of the last named yield an essential oil, which has been examined by Ferrand and Bonnafores (*Bull. Sci. Pharmacol.*, 1913, **20**, 403), who found it to consist principally of a terpene with a small amount of an oxygenated body not yet identified.

**RESEDA.**—See “Mignonette.”

**REUNIOL.**—This is a name given to an alcohol, or mixture of alcohols, isolated from Réunion geranium oil. It is, however, only an impure form of geraniol (mixed with citronellol).

**RHODINAL.**—Rhodinal,  $C_{10}H_{18}O$ , is the aldehyde corresponding to the alcohol rhodinol. It is isomeric with citronellal, and probably has the constitution  $(CH_3)_2C:CH.CH_2.CH_2.CH(CH_3).CH_2.CHIO$ . It had for many years been considered that the alcohol rhodinol (*q.v.*) was merely a mixture of geraniol and citronellol, but it is now clear that rhodinol and citronellol are two isomeric alcohols, their corresponding aldehydes being rhodinal and citronellal. The individuality of the two aldehydes has been confirmed by the researches of Harries and Himmelmann (*Berichte*, 1908, **41**, 2187). These chemists showed that commercial “citronellal” yields different results when treated with ozone, according to the source of the aldehyde.

H. J. Prins (*Chem. Weekblad*, 1917, **14**, 692) has also isolated two isomerides from commercial specimens of citronellal, which have the following characters:—

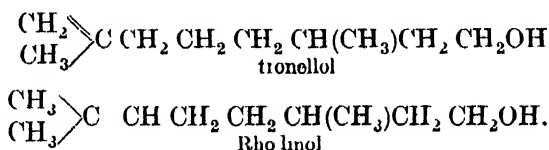
|  | 1.        | 2.        |
|--|-----------|-----------|
| Boiling point . . . . .                  | 203°–204° | 198°–199° |
| Specific gravity at 14° . . . . .        | 0.888     | 0.8745    |
| Melting point of semicarbazone . . . . . | 85°–86°   | 83°–84°   |

Commercial citronellal thus appears to be a mixture of the two isomeric aldehydes citronellal and rhodinal.

**RHODINOL.**—Rhodinol, an alcohol of the formula  $C_{10}H_{20}O$ , is a compound over which considerable controversy has raged for many years in the chemical world. (See “Citronellol.”) It was originally announced by Eckart to be the essential alcoholic constituent of otto of rose, and was regarded by him as being an unsaturated open-chain alcohol.

Markovnikoff about the same time claimed that an alcohol

which he termed roseol was the principal odorous ingredient of otto of rose. In 1894, Bertram published results which claimed to show that both these bodies were merely geraniol. In 1896, Tiemann and Schmidt showed that the alcohols of otto of rose were a mixture of geraniol and citronellol, and suggested that the last named body had been mistaken for "rhodinol" and "roseol." Up till fairly recently the evidence available indicated that rhodinol was, in fact, nothing but impure citronellol. But recent investigations have conclusively proved the identity of rhodinol as an isomer of citronellol. The two bodies do not appear to be stereoisomeric, but they are in all probability structurally isomeric. They probably have the following constitutional formulae:—



From a perfumer's point of view, the difference between the two bodies—and, of course, their esters—lies entirely in their odour values. The bodies citronellol and rhodinol and their esters, as met with in commerce, are always, or almost always, mixtures of the two isomers. The alcohols, as obtained from various sources, whether called citronellol or rhodinol, have the following average characters:—

*From Rose Oil*

|                         |           |
|-------------------------|-----------|
| Boiling point at 15 mm  | 113°-114° |
| Specific gravity at 20° | 0.8612    |
| Refractive index        | 1.4579    |
| Optical rotation        | — 4° 20'  |

*From Geranium Oil*

|                                 |           |
|---------------------------------|-----------|
| Boiling point (normal pressure) | 225°-226° |
| Specific gravity at 15°         | 0.862     |
| Refractive index                | 1.4569    |
| Optical rotation                | — 1° 40'  |

*From Citronella Oil*

|                       |          |
|-----------------------|----------|
| Boiling point at 7 mm | 109°     |
| Specific gravity      | 0.862    |
| Refractive index      | 1.4575   |
| Optical rotation      | + 2° 32' |

## P E R F U M E R Y

### *From Barosma Pulchella Oil*

|                        |       |          |
|------------------------|-------|----------|
| Boiling point at 6 mm. | . . . | 93°-95°  |
| Specific gravity       | . . . | 0.8723   |
| Refractive index       | . . . | 1.4629   |
| Optical rotation       | . . . | + 2° 14' |

### *By Reduction of Citronellal*

|                           |       |           |
|---------------------------|-------|-----------|
| Boiling point at 17 mm.   | . . . | 117°-118° |
| Specific gravity at 17.5° | . . . | 0.8565    |
| Refractive index at 17.5° | . . . | 1.4566    |
| Optical rotation          | . . . | + 4°      |

An optically inactive rhodinol has been prepared by Bouveault and Gourmand from synthetic ethyl rhodinate.

The alcohols citronellol and rhodinol have faint but sweet rose odours, and it may be taken for granted that practically all commercial specimens of either alcohol—*eo nomine*—are really mixtures of the two alcohols in varying proportions. And as such commercial specimens of the alcohols are the basis for the preparation of esters of the alcohols, it is equally true to say that the esters of citronellol or rhodinol are also mixtures of isomeric esters.

**RHODINYL ACETATE.**—This ester is supplied commercially as an artificial compound for use in rose and bergamot compositions. As will be seen by reference to the monograph "Rhodinol," it is undoubtedly a mixture of the acetates of the isomeric alcohols citronellol and rhodinol. The commercial article is one which must largely be judged on its odour, but of course, on saponification it should give results which indicate the presence of from 90 to 95 per cent. of esters of the formula  $C_{10}H_{19}O.OO.CH_3$ . It should have a specific gravity about 0.900, and a refractive index about 1.4500. It is of considerable value in soap perfumery, and is also of value in ordinary perfumery, both as a fixative, and because it imparts a floral-fruity odour to perfume mixtures.

**RHODINYL BUTYRATE.**—This ester, corresponding with the acetate (*q.v.*) has a distinctive rose odour, which renders it of great value in the preparation of artificial otto of rose. It is, like the acetate, a mixture of isomeric substances. Its specific gravity is about 0.896; refractive index, about 1.4555; and boiling range from 260° to 270°.

**RHODINYL FORMATE.**—This ester is, like the acetate and

butyrate, a mixture of isomeric substances. It is of a sweet rose odour, and is useful in giving a special "note" to artificial otto of rose, and also in the preparation of floral bouquets generally.

**RHODINYL PROPIONATE.**—This body, which commercially is a mixture of isomers, as are all commercial esters of rhodinol, has a specific gravity 0.911; refractive index, 1.4570; and boils at about 255°.

**RHODIUM OIL.**—Genuine rhodium oil, or oil of rosewood, is probably obtained from the wood of *Convolvulus scoparius* and *C. floridus*, belonging to the natural order *Convolvulaceæ*, shrubs growing in the Canary Islands. The genuine oil has long ceased to be a commercial article, and oil of rhodium to-day appears to be a mixture of cedarwood, sandalwood, palmarosa, and geranium oils, to which a very small amount of otto of rose may or may not be added. J. H. Gladstone (*Jour. Chem. Soc.*, 1864, 17, 1) examined a sample of the oil, but it is uncertain whether it was a genuine sample or not. He found it to be a thick yellow oil of specific gravity 0.906, and optical rotation about  $-6^{\circ}$ . He considered it to contain 80 per cent. of terpenes (probably sesquiterpenes). Schimmel & Co. (*Bericht*, April, 1887, 28) distilled a sample from wood of unauthenticated botanical origin, and found it to have a pleasant rose odour, and to congeal at  $+12^{\circ}$  to needle-shaped crystals. Schimmel & Co. also distilled a sample from material originating from Teneriffe (*Report*, April, 1889, 37), and which resembled the wood of *Convolvulus scoparius*. The oil obtained had a specific gravity 0.951; optical rotation,  $+1^{\circ}30'$ ; acid value, 0; ester value, 0; and ester value after acetylation, 151.3. It therefore contained a large amount of free alcohols. (Refer to *P. & E. O. R.*, 1911, 29; 1912, 224.)

**RHODODENDRON OIL.**—From the leaves and flowers of several species of rhododendron (natural order *Ericaceæ*) Haensel (*Chem. Zentral*, 1906, ii., 1495; 1907, i., 1332) obtained 0.123 per cent. of essential oil of a yellow colour and pungent aromatic odour. It had a specific gravity 0.864, and optical rotation,  $-4.33^{\circ}$ . The oil contained traces of an aldehyde, some esters and free alcohols, and probably terpenes. The woody stems yielded about 0.01 per cent. of an essential oil of similar odour. Roure-Bertrand Fils (*Bulletin*, April, 1920, 4, i., 34) state that the young shoots of the rhododendron known as the "laurel-rose" of the Alps (probably *R. ferrugineum*) have an odour of pine needles. From these shoots they obtained 0.17 per cent. of

## PERFUMERY

essential oil of a balsamic odour which had a specific gravity 0.840; acid value, 0; and saponification value, 63.5.

**RHYUNO OIL.**—This oil is one distilled in Japan from material of unknown botanical origin. It contains about 75 per cent. of safrol, so may be of value for the preparation of that body for heliotropin manufacture.

**RONDELETIA.**—The perfume sold under the name "Rondeletia" was in Victorian days one of the most popular handkerchief perfumes on the market. To-day it has been largely displaced by perfumes with more decided odours. As sold, no perfume of this name has, and probably few ever had, any real connection with the delightfully fragrant flower which provides the name. Mixtures of bergamot, lavender, cloves, and sandalwood oils, modified with some floral extract have usually been sufficient to pass muster for rondeletia. The name, however, was given by the botanist Plumier to an extensive West Indian and tropical American genus of the *Cinchonaceæ*, in honour of Rondelet, a well-known physician and natural historian. The principal odorous members of the genus are the following (Sawer, "Odorographia," ii., 459): *Rondeletia odorata* is a shrub 5 or 6 feet high, a native of Mexico and Havana, and is found on rocks of the sea-side. The flowers are of a scarlet colour, and are very sweet scented, probably being the original flower which provided the name for the popular perfume. *R. discolor* is a native of New Granada, with fragrant flowers. *R. disperma* is found in the woods of Cartagena, and is very common in the islands of Baru and Tierra Bomba. The flowers are of a purplish-white colour, and are sweet scented. *R. exserta* is a native of the interior of Bengal, and has been found particularly over the ruins of the ancient city of Gour. It is also found in the dry forests of the tropical Himalayas, from Chenab eastward to Nipal and Sikkim. The flowers are white and fragrant.

**ROSE, THE PERFUME OF THE.**—Probably no perfume has been so persistently popular as that of the rose. And whilst no synthetic perfume has ever been able to displace the natural perfume, as has practically been the case with the violet perfume, efforts to manufacture an artificial rose perfume have been unremitting. It may, however, be at once said that there is no "artificial" otto of outstanding merit which does not contain a substantial amount of natural otto of rose; and it is also true that the bulk of the artificial rose perfumes are made up of



natural isolates—various constituents of other essential oils which are identical with constituents found in natural otto of rose, the actual synthetic substances used in such artificial mixtures being but a small proportion of the whole. This point will be dealt with later.

So important is the rose industry that numerous scientific treatises have been written dealing with the history, botany, cultivation, and chemistry of the rose. Although, as will be seen in the sequel, the industry is, in the main, in the hands of the Bulgarians, the scientific knowledge of the rose—other perhaps than the chemical—has been mainly developed by Frenchmen. The following are perhaps the most important of the scientific treatises dealing with the flower J. P. Buchoz, "Monographie de la Rose," Paris, 1804, M. Bortard, "Manuel complet de l'amateur de Roses," Paris, 1836, R. Blondel, "Les produits odorants des Rosiers," Paris, 1889. To these works much of the information available up to 1889 contained in the present monograph is due.

Herodotus is probably the earliest writer to differentiate between the odours of various roses, referring to the "sixty-leaved rose as having a finer odour than others" ("Histories," bk. iii., ch 138). It is probable that he was here referring to *Rosa centifolia*. Amongst the Romans rose leaves were regarded as an antidote to the headaches, etc., resulting from an excess of wine. This probably accounts for the practice of causing rose leaves to rain down on the guests at the end of a feast, and also of the practice of steeping rose leaves in wine.

The use of the rose leaf as a source of perfume is, of course, very ancient, and the use of perfumed leather (how the perfume was imparted from the leaves to the leather is not known) was at a very early date introduced from either Greece or Babylon to Rome. But it was in the form of rose water, prepared by maceration of the leaves, or by some similar process, that the Romans chiefly enjoyed the perfume of the rose. Apparently the supply of roses was originally brought from Egypt to Rome, and the principal rose so imported appears to have been *Rosa damascena*. But this supply was not adequate, so that the cultivation of the rose in Italy became popular. Virgil has mentioned the famous rose gardens at Poestum ("Georgics," iv.) in the verses—

"Forsitan et pingues hortos quæ cura colendi  
Ornaret, canerem, biferique rosaria Poesti"

Pliny, however, appears to be the first to describe roses in

such a way as to be of any botanical assistance to the modern student. He ("Natural History," bk. xxi., ch. iv.) divides roses into wild and cultivated flowers, and classifies them according to their colour, odour, and habitat. He appears to have known the roses which we now know as *Rosa gallica*, *R. centifolia*, *R. damascena*, *R. provincialis*, and *R. moschata*, and he is certainly the earliest observer to have noted that the leaves of *Rosa rubiginosa* had an odour resembling that of cinnamon.

Charlemagne, in his "Capitularies," recommends the cultivation of the rose, and in his time the flower, both as a perfume and as a flavour, became of importance in upper-class households.

The first mention to be found in a European work of a distilled rose water is in a work by Joannes Actuarius ("De methode medendi," bk. v., ch. iv.), which appeared towards the end of the thirteenth century. Towards the end of the sixteenth and at the commencement of the seventeenth century the essential oil of roses was discovered, and it is no exaggeration to say that the pharmacopœias of the sixteenth, seventeenth, and eighteenth centuries contain a very large proportion of their medicaments flavoured with rose water, powdered roses, or essence of rose.

The history of the rose in perfumery on a modern basis dates, of course, from some time after the discovery of the method for isolating the essential oil. It is here necessary to call attention to the fact that the odorous constituents of the rose possess very varying degrees of solubility, so that, as the flowers are of necessity distilled with water, the actual odorous constituents divide themselves into (a) the amount of various ingredients necessary to saturate the distillation waters, and (b) the residue, which constitutes the greater part of the odorous constituents, which does not dissolve in the water. But as these constituents vary enormously in solubility, it results that rose water and oil (or "otto") of rose differ considerably in odour. This is, in the main, due to the high solubility of the body phenyl-ethyl alcohol, which almost disappears from the oil and is almost entirely dissolved by the distillation water.

The art of distilling the rose undoubtedly had its origin in Persia. According to Ibn Khaldun, about 810-817, in the reign of the Caliph Mamoun, the province of Farsistan was compelled to provide annually a tribute of 30,000 bottles of rose water to the treasury at Bagdad. Istakhri ("Le Livre des Campagnes," p. 73) refers to the considerable production of rose water through-

out the province of Farsistan, which was exported to China, India, Egypt, Spain, and Morocco. The principal seats of manufacture were at Dschur (the Firuzabad of to day), between Shiraz and the coast, where the rose industry is still in existence. The Arabs were responsible for the introduction of the distillation of roses into Europe. The Calendar of Harib for the year 961 refers to April being the most suitable month (in Spain) for the preparation of rose water. Kaempfer (\* Amoenitates 1712) speaks with admiration of the roses of Shiraz and of the considerable trade in their products. He says: Distilled rose water is freely carried all over India and the provinces of Persia itself. It is esteemed as an article of luxury at feasts and reunions of friends. It is boiled with cinnamon and white sugar, and is drunk as an alternative to *kahua*. Rose water is used to sprinkle the guests with as a sign of welcome. It is more expensive than wine. The roses themselves are also expensive.

The rose has no special name in Persia. It is called *gul*—the flower *par excellence*. Kaempfer describes a garden of roses at Persepolis, the rose cultivated being apparently *Rosa moschata*. He also gives the first positive indication that we have of the definite existence of an industry for the distillation of essence of rose which was also made at Shiraz. About 1574, Geronomo Rossi (De distillatione libri Rayenna 1552) had noted that one could separate an extremely odorous oil matter from the surface of rose water. Angelus Sili (\* Opera Medicochymica Frankfort) refers between 1610 and 1630 to the volatile oil of roses as a substance 'of brilliant whiteness, resembling spermaceti'. Poinet towards the end of the same century, refers to the sale of a small quantity in Paris. 'Besides,' he states, 'the water which one obtains from roses one can extract an odorous inflammable spirit, most useful for fortifying and rejoicing the heart and stomach.'

It is clear then that by the end of the sixteenth century oil of rose was known to the chemists and apothecaries of Europe. Although the East is the original home of the rose and its perfume, it was only about the same time that the separation of the essential oil was discovered there. Langles (\* Recherches sur la découverte de l'essence de Roses 1804) fixes the date of the discovery in the East as 1612. He searched Persian and Mongolian literature, but found no mention of *Alhr gul* (fat of the flower—essence of rose) anterior to that date. The Persian poet Hafiz often speaks of *gulab* (rose water) but never of *alhr* (essence). In the famous

*gulistan* (rose garden) of Sadi this is also true. Nor do any of the European travellers who visited Persia before 1612 ever mention essence of rose although frequently referring to rose water. The essence is first described in a work entitled "*Tariykh montekheb lubab*," a history of the Grand Moguls from 1525 to 1667, written in Persian by Mohammed Achem. He mentions the essence twice, firstly in a chapter entitled "*Marriage of the Princess Nour Dghan with the Divine Dghan Guvr*." Inventions and Discoveries of the Queen of the World, where it is stated "The essence of roses which Nour Dghan Beygum first called essence of Dghan Guvr, as well as perfumes of lesser value which those less favoured by fortune may use, was invented by her and her mother."

The second reference is in the chapter entitled "History of the seventh year of the reign of Dghan Guvr, and the feast of the New Year, whose magnificence astonished the world, corresponding to the year of the Hegira 1021." In this chapter the following account of the essence occurs: "At the commencement of the perfumed feast of the New Year and of this year of the reign the mother of Nour Dghan having presented to the Prince some essence of the rose water which she had prepared and the Prince having found it agreeable he decided to attach to it his illustrious name and called it *Athr Dhanguvt*. He also presented to the Princess a necklace worth 30 000 rupees. For this was in truth a wonderful discovery no odour compared with this, etc. etc."

Manucci (*Histoire Generale de l'empire Monghol depuis sa formation jusque a present* 2nd ed., vol. 1 p. 326) gives the following as the circumstances of the discovery of the essence: "It was at a feast given by this ambitious and clever woman to her illustrious husband that essence of rose was discovered. Amusements and rejoicings were on a prodigal scale on this occasion. The princess indulged her luxurious caprice so far as to have a canal circulating round the garden filled with rose water. Whilst the emperor was walking with her along the banks of this canal, they perceived a kind of scum floating on the surface of the water. They gathered this from the edge of the water and realised that it was something from the roses which the heat of the sun had caused to separate from the water (through evaporation) and to aggregate in a small mass. Everybody agreed that it possessed the most delicate perfume known in India. As a result this chance discovery was turned to useful purpose, and the art of distilling the essence resulted."

## PERFUMERY

Whatever be the truth of such legends, there is no doubt that this feast took place in the year 1612, and that the manufacture of essence of rose in Persia dates from the same year. In 1684, when Kaempfer visited the country, the distilleries of Shiraz were in a very prosperous condition. He mentions the practice of adding sandalwood shavings to the roses on distillation for the purpose of improving the odour (!). A century later Colonel Polier records the same fact, but truly states that so far from improving the odour of the essence of roses, it diminishes its quality and fineness (Polier, "Asiatic Researches," i., xvi.). Rose water prepared when the essence was distilled in this manner was sold under the name *Ssandalî gulab*. Forster, about this period ("Voyages de l'Inde à Pétersbourg," i., 294) mentions the roses of Cashmire as the most beautiful in the world, and refers to the essence as being particularly appreciated. At the commencement of the nineteenth century, Olivier ("Voyage dans l'Empire Ottoman," 1807, v., 367) found the industry in full swing in Shiraz, Farsitan, and Karman. The distillation of essence of rose appears to have been introduced from Persia, *viâ* Bassorah, and from Arabia into India, first to the town of Kanauj, on the Ganges, which is non-existent to-day, and then to Ghazipore, where the industry is still in existence. It is through the Turks that the industry of the distillation of roses came to Europe. Essence of roses was distilled in the island of Chios and in Smyrna at an early date, and, according to a tradition still current in Bulgaria, it was from Tunis that the industry was brought to Kazanlik by a Turk in about 1680. About the same time the distillation of roses was introduced into France from the African coast.

We may now turn to the industry as it exists at the present time. It is obvious that conditions of soil and climate such that good harvests of roses can be obtained are the first necessity for the production of essence—or otto—of rose. This, however, is by no means sufficient, as the most extraordinary differences are to be noted in the amount of otto yielded by the same roses when grown in different districts. So important is this point, that as a matter of fact the world's supply of otto of rose is confined to districts within very narrow limits.

The most important source of supply is Bulgaria, which provides the greater part of the world's consumption of otto of rose. The most important centre of production is in the region of the Balkans, in the district originally known as eastern Roumelia

## PERFUMERY

space of 6 feet is left between each row. The propagation is not effected by means of cuttings or layers, but by cutting down entire bushes. These are pulled up and chopped into pieces. The stump, with as much root as possible left attached, is torn up and divided with a hatchet, and the pieces are planted with their boughs and leaves left entire, four or five abreast in long trenches about 18 inches wide and deep, and dressed with manure and well watered. This is done in October or November; the young shoots appear about April, when the ground is well weeded and the mould raked high up to protect the young plants from the cold. In May a few flowers will be obtained, and by the next year they will be in full bearing, the flowering attaining a maximum in the fifth year. After a life of ten years most cultivators prune the plants right down to the ground, and new branches and often flowers will appear the following year.

The harvest commences about the third week in May and lasts from twenty to thirty days. It is most rapid in very hot summers, perhaps lasting only from sixteen to twenty days, but with mild temperature and soft rains the harvest will be prolonged for a full month. Gathering commences at daybreak and lasts until about ten o'clock, and if the day be cloudy it may go on all day. For it is very necessary that the flowers be not picked with the hot sun on them. A very short harvest means picking the flowers during the heat of the day, which impairs the fragrance of the resulting otto, and also entails leaving the picked flowers in the heat of the sun, since the distilleries are unable to deal with them fast enough, with the result that partial fermentation sets in and the otto distilled is of a poor quality.

The flowers are now carried straight to the distilleries. In the large centres these are usually built six to ten in a row under sheds open on one side, whilst in the outlying districts the stills of the peasants are put up temporarily in a thatched shed. Many peasants, either through the want of water or through lack of any capital, are unable to distil their own flowers, so that they are compelled to sell them to the nearest distillery.

The stills used for distillation are made of sheet copper, in the shape of a truncated cone. The body is about 3 feet 6 inches in height, composed of two pieces joined in the middle by a tinned band. The diameter of the body is here about 2 feet 6 inches, and of the neck about 10 inches. The head is of the shape of a mushroom top, about 1 foot in height, leading by a tube to the condensing tube, which passes through a wooden tub, through

## PERFUMERY

which cold water is kept running. The method of distillation is as follows: A charge of about 25 lb. of flowers is introduced into the still with about 16 to 18 gallons of water, when about 2 gallons of liquid has distilled over, the still is opened and the flowers taken out, a fresh charge of flowers is introduced, the water made up to the original quantity, and a fresh distillation commenced.

The distillates are mixed and redistilled, the otto floating on the surface of the latter distillation being allowed to separate, when it floats on the water. It is separated from this by a small conical funnel which has a tiny hole at the end to allow the water to drain away.

If the otto be skimmed off the first distillation water it differs somewhat in odour and general character from that obtained by the second distillation.

If, again, the otto be distilled in steam stills without a naked fire being allowed to touch the flowers at all, a still different product is obtained.

These differences are to some extent explained by the fact that certain constituents of the otto are soluble in water, and therefore the more water used in the process the more of the soluble constituents are removed from the otto.

The rose water produced as a by product is of fine odour, but the expense of carriage, etc. prevents it from entering into commerce as a competitor with the French rose water.

The rose cultivated in Bulgaria is the common red rose, *Rosa damascena*. The white rose, *Rosa alba*, is grown, but almost entirely in the form of hedges to separate different properties, but as the white rose yields an otto, although less odorous than that of the red rose, it is frequently distilled with the latter. In addition to the primitive stills described above, there are a few modern steam stills at selected centres of the rose districts, but these can, obviously, only deal with rose flowers which are grown sufficiently near to the town in which the modern distillery is situated to be brought so rapidly to the stills that no decomposition of the flowers has set in. It is obvious, therefore, that the bulk of the flowers must be dealt with in the primitive stills owned by the peasants.

We may now turn to the otto of rose industry in India—not because it is of the same commercial importance as the industry in France or Anatolia, but on account of the attempts to develop the essential oil industry within our own Empire and Dependencies.

## PERFUMERY

For upwards of two centuries rose distilleries have existed at Ghazipur, in Lahore, and at Amritsar. The essence is entirely consumed locally. The harvest commences in the middle of February or March, and finishes in April. The Indian otto of rose question has been studied and reviewed by Gadre and Muckerji (*Journal of Indian Industries and Labour*, 1922, i., 86).

The United Provinces Government instituted in 1920 an investigation into the rose industry of the provinces with a view to suggesting necessary improvements for the betterment of this branch of the perfume industry. During two previous years the experiments were conducted by the Indian Essential Oils Co., of Cawnpore, while the industrial chemist to the Government of the United Provinces attended during some of their last year's experiments. In their first report on these experiments the firm obtained a yield of 0.0045 per cent. otto from rose flowers in Aligarh district, using the common Deg still. In their second report, viz., on the 1921 experiments, the same firm obtained a greatly enhanced yield by improvement in distillation apparatus, whereby they obtained as much as 0.025 per cent. otto on the weight of flowers and also indicated the possibility of obtaining as high a yield as 0.03 per cent. with further improvements in apparatus, thus bringing the yield nearly up to the level of the Bulgarian rose industry of the present day. From the above data the prospect of the Indian rose industry appeared to be quite hopeful only with the substitution for the Deg still of some such improved still as that used by the Indian Essential Oils Co., although they recommended that the "agricultural and botanical aspects of the problems should be studied," since a further improvement in the quality of the flower would be welcome. The ratio between the efficiencies of the Deg still and the improved still constructed by the firm was shown to be—yield of otto from Deg : yield of otto from improved still :: 0.0045 : 0.015, or 3 : 10. These reports gave no idea, however, as to the way in which the percentage yield of otto was determined, nor were any comparative determinations made on flowers from the different rose centres in the United Provinces.

It was therefore decided during 1922 to repeat the experiments, using rose flowers from Hathras and Barwana in the Aligarh district, Ghazipur and Cawnpore, trying types of stills other than those used during the previous experiments to obtain comparative results. The flowers used for these experiments were *Rosa damascena*.



Flowers from Hathras were obtained by the Indian Essential Oils Co., preserved by means of common salt, packed in tins, and sent down to Cawnpore by rail. These flowers were distilled by the firm at their factory in Cawnpore, and the distillates sent down to the Government Technical Laboratory, Cawnpore, for examination: they used the Deg, their improved still, and the steam still. At the Government Technical Laboratory, flowers grown in Cawnpore were distilled by (i.) a steam still, and (ii.) a direct-fired still which was a modernised improvement of the Deg still. Arrangements for the distillation of Ghazipur flowers could not be made. But, for the sake of comparison, rose water of different concentrations, distilled by a reliable Ghazipur firm, was obtained and examined.

The roses round about Cawnpore flower in March and continue to flower through April. The experimental distillations commenced on April 1st, 1921, and extended right through the month, the total amount of flowers distilled being 37 to 38 maunds. The maximum atmospheric temperature during the duration of the experiments was about 108° F., and the minimum 78·5° F.; the humidity being, on an average, 35. There was no high wind, but *loo* (draughts of hot air) was prevalent on some days. Altogether it was a particularly trying season in which to prepare rose otto; these months of March and April have always been the season *par excellence* for conducting the distillation of rose flowers. The roses belonged to the species of *Rosa damascena* Mill—perhaps the commonest Indian garden rose—and were of the red or pink variety exclusively. The flowers were collected early in the morning, brought over to the laboratory, and distilled as soon as possible—about nine o'clock; on some occasions the distillation could not start early owing to the late arrival of the flowers, in which cases the operation would begin by eleven o'clock.

The methods used in the experiments were an improvement over the time-honoured and wasteful processes in vogue among the small distillers of this province. At the outset the flowers were distilled in the steam still in lots varying from 80 seers to so small a batch as 15 seers, the same weight of distillate being collected as of the flowers put in. The practice in Asia Minor is different. There, from 1 oke of rose flowers, 2 okes of rose water are collected. The distillation generally occupied from three to five hours. This gave the once-distilled rose water, which finds greater demand than more concentrated water, probably owing to its cheapness.

## PERFUMERY

Rose flowers grown for purposes of distillation at places like Hathras, Sikandra Rao, Hasayan, Barwana, and other places thereabout in the Aligarh District are superior to those available at Cawnpore or Ghazipur for the purpose. The flowers can, with the use of a preservative like common salt, be stocked undamaged for distillation purposes for three or four days after they are plucked. The superiority of the roses cultivated in the Aligarh district appears to be due to the richer soil and better irrigation facilities in that district. The high results for percentage yield of otto obtained by the Indian Essential Oils Company last year, as mentioned in their report, could not be substantiated by the authors; the average calculated yield of otto did not exceed 0.015 per cent. The optimum yield of otto obtainable from these flowers was found to be much lower than that known to obtain in Bulgaria and elsewhere.

Live steam is unsuited for making otto from rose flowers. A steam-jacketed still would be ideal, but its use may not be practicable on rose fields and with all grades of distillers.

The rose industry is of considerable importance in France, and enormous quantities of flowers are grown for perfume purposes. The bulk of the perfume is extracted in the form of pomade, absolute, or concrete, but a considerable amount of otto of rose is also prepared. When absolutely pure, French otto of rose is of such fine odour that it is largely consumed in the country, and only a comparatively small amount is exported. For the following details of the French rose industry acknowledgment is made to M. Jean Gattefossé. He states that France is really the pioneer in the art of rhodology, and says:—

“It is true that in the thirty years 1872-1902 German rose growers produced 115 new varieties of roses which were taken up by the French cultivators, but in the ten years 1903-1913 they took no less than 238 new roses from France. To all the German roses a counterpart, equal and frequently superior, is to be found amongst the French productions.

“The cultivation of the rose is a very old industry in the Grasse district, and the flower has been distilled there and near by for many years. The rose which had up till fairly recently been employed for distillation, almost to the exclusion of other varieties, is the well-known *Rosa centifolia*, usually known as the Rose de Mai. This rose is of exquisite fragrance, but requires much care in cultivation, and does not give a very high yield of flowers. Rose de Mai is of so beautiful an odour that it is almost exclusively

## PERFUMERY

used for enfleurage purposes and for the preparation of rose water.

“Enterprising perfumery experts in the south of France recognised several years ago that there was an immense possibility in all their various roses grown for decorative purposes and grouped together under the general name *roses de jardin*. These roses are cultivated for sale, and are forced during the winter and sold at high prices, being despatched by special trains to the various capitals (that is, before the war). During the spring the natural crop commences, and gradually becomes more plentiful, and the price, of course, falls. The three problems which required solving were: (1) the economical utilisation of the *roses de jardin*; (2) the creation of fresh species which, on account of abundance of flowers, or richness in oil, would become more remunerative; (3) the planting of rose gardens in favourable localities.

“From the month of May onwards the mixed roses of which we have been speaking were practically wasted, and merely fell to the ground to be dug into the soil again. In 1912 attempts were made by various perfumers to utilise them for distillation of otto. The flowers were turned into the stills, or extracted with petroleum, without any consideration of new principles necessary in a new industry. The results were, generally speaking, disappointing, the yields being very low. In 1913 each individual distiller selected the variety which seemed to him to give the best otto or the best yield. Some preferred to use the well known Brunner rose, others Paul Neyron, Paul Nabonand, Van Houtte, Drusky, or tea roses. Now it was clear, at an early stage, that the yield of perfume to volatile solvents was quite remunerative and economical, owing to the abundance of the flowers obtained. Concretes, therefore, from the *roses de jardin* were commercially successful, but one could not say quite the same for the otto distilled. The problem is of a quite different nature, because the stills in different factories differ considerably between themselves, and many are quite unsuitable for the distillation of otto of rose. The elaboration of improved stills has attracted considerable attention, and during the past few years it may truly be said the French rose distiller has succeeded in constructing stills admirably adapted to the distillation of the rose, and which have solved the problem of the economical use of the *roses de jardin* for the manufacture of otto. Of course that is, generally speaking, only true for the larger and up-to-date scientific distiller.

## PERFUMERY

We shall make no attempt to give a catalogue of French roses which are capable of yielding otto on a commercial scale, but will content ourselves with a brief indication of the direction which the cultivator and distiller have taken. Ulrich Brunner is a magnificent cherry-red hybrid perpetual, much esteemed for the beauty of its blooms for decorative purposes. It is one of the favourite varieties of the Côte d'Azur and the Riviera, and its odour is exquisite. On distillation it gives a sweet rose odour, but not so powerful an odour as that from the Rose de Mai. The otto is very solid, rarely melting below  $28^{\circ}$ . Under usual conditions of distillation in the Alpes-Maritimes, about 1 kg. of otto is yielded by 18,000 to 20,000 kg. of flowers; but with specially elaborated stills a considerably higher yield is obtained. Louis Van Houtte is another hybrid perpetual, of an intense maroon-crimson colour, and Marie Van Houtte is a tea rose of an exquisite creamy yellow colour, with a bright rose edge. Both roses are great favourites with growers, and have delicious perfumes. The yield of otto is relatively high, and equals or even exceeds that of the Rose de Mai in stills of suitable construction. The otto of the Van Houtte roses is distinctly green in colour when freshly distilled, but becomes yellow on keeping. Its odour is quite different from that of the otto from the Rose de Mai. It can only be described by saying that it recalls the perfume of a bouquet of mixed roses, such as one is accustomed to find in use for decoration purposes. This otto usually melts at a low temperature—from  $15^{\circ}$  to  $16^{\circ}$ —and has a particularly high optical rotation, frequently reaching to  $-10^{\circ}$  or  $-11^{\circ}$ . Its ester value is about 10. A blend of the ottos from the Brunner and Van Houtte roses is exceedingly sweet in odour. Another distillation favourite is Paul Nabonand, but, so far as we are aware, it has never been distilled without some admixture of other roses, so that its particular type of otto can scarcely be described. Gattefossé, however, has distilled on a commercial scale roses of which the large majority were Paul Nabonand, so that the otto obtained may be said to be approximately that of this rose. It has a specific gravity 0.855 at  $30^{\circ}$ , and melts at  $19^{\circ}$ . Its optical rotation is about  $-2^{\circ}$ , and its ester value is very high—up to 42.

“Other roses distilled for their otto, mixed with their garden companions, are: Paul Neyron, Souvenir de Malmaison, Maréchal Neil, La France, Gloire Lyonnaise, Comte Bobrinsky, Gabriel Suizet, and Frau Carl Drusky, and there is another rose quite of the first rank, an exceedingly beautiful offspring of La France,

## PERFUMERY

obtained by that skilful cultivator, M Jules Graveraux which has received the glorious name 'La France Victorieuse'

"The question of the creation of new roses which will yield payable quantities of otto is, of course, still in its infancy, and we shall only mention the rose cultivated in the bagatelle garden of MM Graveraux and Cochet Cochet and which has been named 'Rose d'Hai' This comparatively new rose has a flower of a purplish-red colour, and blooms abundantly and for a very prolonged period—from three to five months, according to conditions of temperature, etc We have had the opportunity of examining a sample distilled entirely from these flowers, and find it to have an extraordinarily low melting point This is about 7 to 8 thus indicating a very low stearoptene content, and a correspondingly high amount of odouriferous constituents Its specific gravity is, as would be expected, very high—up to 0.875 or 0.880—and its optical rotation is about  $-2^{\circ}$ "

Anatolian otto of rose is produced in fair quantities and is practically identical with ordinary Bulgarian otto

For some few years past there has been a commercial utilisation of the rose flowers growing naturally in the valley of Lake Burdur, in the interior of Asia Minor

Later, several peasants who owned land, seeing that the growing of roses for the production of essence was likely to be remunerative, began little by little to plant rose trees so that the area under cultivation is now much extended

Lake Burdur is situated between the town of that name and Isbarta This latter is the ancient Sparta of Pisidia, which was a flourishing town in the days of Alexander the Great The whole of this district is inhabited by an essentially agricultural population, who own land of magnificent fertility. The climate is mild, and the valley, protected by the mountains against cold and frost, is most favourably situated for the culture of roses

Most of the peasants own stills for the distillation of their flowers, while there are other cultivators in a rather better position, who buy up the roses of those whose production is very small and who possess no distillation apparatus of their own

The total output of otto of rose from the Anatolian districts appears to be from 200 to 350 kg annually The greater part of this is derived from roses cultivated from plants originally grown in Bulgaria. But in the Broussa district a native rose known as the "Rose Hafis" is grown, and yields otto of a quite similar character.

## P E R F U M E R Y

For a full account of the Anatolian industry (which does not in any essential matter differ materially from the Bulgarian industry), see a report by Bredemann, "The Otto of Rose Industry in Asiatic Turkey," *Schimmel's Bericht*, 1917, 45.

Although small amounts are distilled in various other parts of the world, it will be sufficient to describe their characters, as there is nothing specially characteristic in reference to the methods of cultivation or production.

It is only a very few roses that are cultivated for distillation, so that there is not much variety in the natural rose odours available to the perfumer. He is, however, called upon to imitate the odours of roses which are not, in fact, available for natural perfume material, and in this task he is obliged to rely on the use of artificial perfumes to give the necessary "note" to his production. Several attempts have been made to classify the various rose odours, but none with striking success. The first such attempt appears to have been published in an American journal ("Varieties of Perfume in the Rose," *The Gardener's Monthly and Horticulturist*, Philadelphia, xxviii., 1886, 249). This classification, however, had little scientific basis, and is not of much use as a guide.

Blondel, in 1889, attempted to group the rose odours in the following ten categories:—

(1) Typical rose odour: characterised by such roses as *Rosa damascena*, with three similar "shades": (a) moss rose; (b) tea roses, characterised by the Maréchal Niel rose; and (c) hybrid roses of the General Jacqueminot type.

(2) Odour of musk: typified by the hybrid moss rose Salet.

(3) Odour of mignonette: *Rosa canina*, *R. sspium*, *R. alpina*.

(4) Odour of violets: *Banksia alba*, Isabella Nabonand.

(5) Odour of lily of the valley: *R. Ripartii*.

(6) Odour of hyacinth: Rose Unique jaune (a Noisette rose).

(7) Odour of fruit: Socrates, Duprez, *R. bracteata*.

(8) Odour of bugs: *Rosa lutea*, *R. platyacantha*, *R. Beggeriana*.

(9) Odour of clove: *Rosa caryophylla*, *R. moschata*, *R. Brunonii*.

(10) Odourless: *Rosa inodora*.

The leaves of a number of roses possess odours which differ considerably from those of the flowers of the same plant.

Generally speaking, the rose odours which the perfumer has to deal with are the following:—

(1) The old-fashioned "cabbage rose" odour, reproduced as

well as may be by the otto of rose from *Rosa damascena* or *Rosa centifolia*.

(2) Sweet briar or eglantine leaves ; isobutyl phenylacetate is usually employed in this perfume.

(3) *Banksia* roses, with the odour of violets. In this the use of minute quantities of artificial violet of the ionone group and of one of the artificial violet-leaf perfumes, such as methyl-heptine carbonate, is recommended.

(4) Tea roses of the Maréchal Niel type. Very minute traces of orris and of one of the higher fatty aldehydes have been used in this perfume.

(5) Musk rose. Here, very minute traces of one of the artificial musks are employed.

E. M. Holmes (*P. & E. O. R.*, 1911, 101) directs attention to the following groups of roses having popular perfumes, and which may possibly be imitated :—

(1) Of the *R. centifolia* group, the Old Cabbage rose, the Maiden's Blush, and the White Cabbage rose, or Unique, are particularly sweet. These only flower in June.

(2) Of the hybrid perpetual or damask rose group the greatest favourite is, perhaps, General Jacqueminot, a rose of bright colour, beautiful form, and delicious odour, that forms the earliest red rose in spring used for buttonholes. This is presumably the "Jack" rose of American perfumers. Victor Hugo is a similar rose, which flowers freely in the autumn. Other sweet-scented roses of this group are Alfred Colomb, Henrich Schultheiss, Hugh Dickson, Lady Helen Stewart, Madame Victor Verdier, Oscar Cardel and Madame Isaac Percire, Horace Vernet, Maurice Bernardin, Pierre Notting, Eugene Furst, and Abel Carriere.

(3) Of the hybrid tea roses, Madame Abel Chatenay holds the first place as a favourite rose for beauty of form, colour, and sweetness, and it is freely produced from June till autumn. La France, Viscountess Folkestone, Caroline Testout, and Pharisaer are all delicately-scented roses belonging to this group. Caroline Testout and Madame Abel Chatenay are two roses formerly largely grown in the celebrated gardens of Holland House.

(4) Of tea-scented roses, Maréchal Niel is a prime favourite, but is a spring rose. Adam, Anna Olivier, Devoniensis, Madame Ravary, and Gloire de Dijon possess varied modifications of the tea odour.

The roses of groups (2), (3), and (4) flower, as a rule, from June until the autumn.

## PERFUMERY

(5) Of the hybrid bourbon roses, *Souvenir de Malmaison*, a good autumn rose, has a peculiarly sweet odour, allied to that of the cabbage rose, but more delicate.

(6) Of the *R. rugosa* group, *Belle Poitevine* and *Conrad L. Meyer* are the most odorous, but the perfume is weak yet characteristic.

There is, of course, no limit to the shades of rose odours, some true to nature, many not so, which the perfumer can produce, but in all cases it will be found absolutely necessary to limit the use of all powerful synthetics to very minute quantities, or the odour will be ruined.

It is of interest to note that the odorous organs of the rose may be divided into two categories—firstly, the petals of the flower; and secondly, certain green parts of the plant, which include the calyx and sometimes the green leaves. These two sets of organs work in the evolution of the perfume independently of each other, to such an extent that no case is known where the perfume of the two organs are identical in the same plant. For example, the *Rubiginosa*, of which the sweet briar is typical, has odourless flowers, whilst its leaves are delightfully fragrant. And when this rose is hybridised, as it has successfully been by Lord Penzance, the so-called Penzance briars (all hybrids) have sweet-scented foliage.

Blondel (*loc. cit.*) has carried out exhaustive researches in order to discover the actual seat of the perfume in the rose, and in so far as the petals are concerned he has shown that the essential oil resides almost, if not entirely, completely in the upper and lower layers of epidermal cells, and practically not at all in the parenchymatous cells included between these two layers. In the green parts of the plant the essential oil is secreted by externally situated glands, which are frequently formed on the teeth of the leaves.

We may now pass on to the consideration of the otto of rose produced in a number of districts in which the rose is cultivated.

As pointed out above, the bulk of the world's supply of otto of rose is produced in Bulgaria. It is obvious that in the distillation of an essential oil which contains constituents of varying degrees of solubility in water, and where the yield is very small compared with the volume of water employed in the distillation, the composition of the oil which separates from the water must of necessity vary according to the conditions of distillation. The bulk of the Bulgarian otto of rose, however, is produced by means of the



primitive stills of the small peasant farmer, under conditions which are practically identical throughout the rose growing villages. Where modern stills are used, the resulting otto may vary from the normal in characters, unless the conditions have been at least approximated to those of the peasant distiller in regard to the relative proportions of water used in the distillation and to the amount of essential oil yielded. It is, however, a very regrettable fact that the amount of otto of rose exported from Bulgaria annually exceeds by a large amount that actually produced in the country. Some years ago adulteration was the rule, and pure otto of rose a rare exception. Owing, however, to the advance in our knowledge of the chemistry of otto of rose, and to the fact that users insist on having their supplies analysed, coupled with the acquisition of Western ideas and education by a number of the better-class Bulgarian exporters, the exportation of pure otto of rose from Bulgaria is far more usual to-day than it was twenty-five years ago. The vases in which it is contained are sealed with the Bulgarian customs seal, but this must never be taken as any guarantee of purity, as it means nothing more than that, if the seal is unbroken, the contents of the vase are in the same condition as when it left Bulgaria. At one time the universal adulterant employed in Bulgaria was the so-called Turkish geranium oil, that is, the palmarosa oil distilled in India and brought to Bulgaria *via* Turkey. To-day this crude adulterant is almost unknown. Pure geraniol and similar compounds are now so easily and cheaply obtainable, and have not the somewhat marked odour of palmarosa oil, that they are employed to-day as the common adulterants. And, unfortunately, certain continental chemists and chemical firms have so far prostituted the science of chemistry as to deliberately prepare artificial mixtures having characters as near to those of the genuine otto of rose as can be obtained, for sale to the ignorant Bulgarian peasants for the express purpose of adding to their otto with the hope of deceiving the analyst. The result of this malpractice is that, instead of only undergoing one act of sophistication at the hands of an unscrupulous merchant, a considerable amount of otto receives at least two "baptisms" before the actual user receives it. As the exporter has to collect numerous small amounts of otto from small peasant distillers living at considerable distances from each other, it is impossible for analyses to be made, and the purchaser relies upon two things. In the first place, pure otto of rose possesses an odour which the expert knows as the "honey odour,"

## P E R F U M E R Y

which is masked, weakened or spoiled by most adulterants. This odour is probably due to the presence of a little phenyl-acetic acid, derived from the oxidation of the phenyl-ethyl alcohol naturally present in the otto. An expert can pick out samples which contain more than a very small amount of adulterant by the odour of the sample, and upon this fact the purchasing exporter relies very considerably. The second point upon which he relies is the melting point and method of congelation of the otto. In the old days of adulteration, when nothing but palmarosa oil was used as the adulterant, the melting point was depressed according to the amount of the adulterant, but as to-day solid substances are also used in order to counteract the depression of the melting point, it is obvious that not much reliance can be put upon the melting point alone. The expert, however, can form a fairly good opinion as to the presence of foreign solid substances from the method of crystallisation of the otto after it has been melted. It is, at any rate, a fact that some of the more expert of the exporting merchants are so able to judge otto of rose in the above manner that they are rarely deceived by a dishonest peasant distiller.

We may now pass on to the chemistry of otto of rose, dealing, firstly, with the composition of the oil, and secondly, with the methods of ascertaining its purity, a portion of the subject of the very highest importance and interest to those who use it.

Of late years much of the controversial matter in reference to the chemistry of otto of rose has been more or less definitely settled, and it will be unnecessary to dwell too much on the earlier, and now admittedly incorrect, work. The following brief summary will fairly well represent the present state of our knowledge of the essence.

Eckart ("Inaugural Dissertation," Breslau, 1891) states that a small quantity of ethyl alcohol exists in the oil. If this is so, which Poleck denies, it is in all probability the result of fermentation taking place in the leaves by keeping them too long before distillation. Markovnikoff and Reformatsky (*Jour. Prakt. Chem.*, 1893, ii., 48, 293) originally stated that the liquid portion of rose oil consisted chiefly of an alcohol of the formula  $C_{10}H_{20}O$ , which they termed roseol. Poleck and Eckart claimed that this alcohol had the formula  $C_{10}H_{18}O$ , and was identical with geraniol. They, however, proposed for it the name rhodinol (which was applied to an alcohol,  $C_{10}H_{20}O$ , from geranium oil by Barbier and Bouveault). Bertram and Gildemeister then showed that the

alcohols from rose oil were in reality a mixture of two bodies, of which they agreed that geraniol  $C_{10}H_{18}O$  was the chief constituent. Tiemann and Schmidt explained these differences, proving that the alcohols consisted of about 75 per cent. of geraniol  $C_{10}H_{18}O$  and 25 per cent. of an alcohol,  $C_{10}H_{20}O$ , which was identical with that obtained by reducing citronellie aldehyde. Hence they naturally insisted on the name citronellol. Much confusion has unnecessarily been caused by various chemists giving names to alcohols they had isolated from different oils in an impure state, and refusing to alter these names after it had been conclusively proved that they were, when pure, identical with already known bodies. Lemonol, réuniol, and roseol are all either geraniol or citronellol or mixtures of them. Rhodinol is, however, now recognised as a definite chemical individual. (See under "Rhodinol" and "Citronellol.")

Traces of esters of these two alcohols and of free acids resulting from their decomposition also occur. The stearoptene was regarded by Markovnikoff as consisting of a single paraffin hydrocarbon of the formula  $C_{16}H_{34}$ , melting at  $37^{\circ}$ , but Schimmel & Co. have separated two hydrocarbons, melting at  $22^{\circ}$  and  $41^{\circ}$  respectively, from the stearoptene. This has been confirmed by Dupont and Guerlain. These chemists suggest that the ester, which appears to be found in larger quantity in French oils than in any other, is an important odoriferous constituent, and is destroyed by repeated distillation with water. They separated the liquid portion of the oil and found it had an optical rotation of  $-10^{\circ} 30'$ , which decreased to  $-7^{\circ} 55'$  after hydrolysis. Charabot and Chiris invariably find rose water acid, which tends to confirm this hypothesis.

Phenyl-ethyl alcohol has recently been shown to be a normal constituent of otto of rose, but it appears to be mostly, if not entirely, lost or destroyed by the Bulgarian method of distillation. This is in all probability due to the solubility of the phenyl-ethyl alcohol in the distillation waters. Nerol is also present in small amount as well as, probably, farnesol, a sesquiterpene alcohol,  $C_{15}H_{26}O$ , present in oil of cassia and oil of cloves. Eugenol and nonylic aldehyde are also probably present in traces. It is possible that the method of distillation by steam vacuum stills in Bulgaria causes the phenyl-ethyl alcohol to be preserved in the otto, and less stearoptene to be brought over. It will probably be necessary to fix fresh standards for this steam-distilled otto as soon as more stills are working in Bulgaria. At present it is only possible to

## PERFUMERY

say that such otto appears to have a much higher specific gravity and refractive index than ordinary otto, and to contain phenyl ethyl alcohol in some quantity.

Turning now to the methods useful for determining the purity or otherwise of otto of rose, one is forced to confess that in practice the determination of physical rather than chemical characters gives us the most reliable information.

The odour of the best otto is always of a type well recognised in Bulgaria under the name "honey odour," which an expert will readily identify.

The value of a pure oil depends on the quality of the flowers used and on the care taken in distillation. It also depends on the amount of solid stearoptene present, for this portion of the oil is quite inodorous.

The value of otto in the locality of its distillation is, as mentioned above, gauged to some extent by its melting point. Consequently, spermaceti, or even paraffin wax, has been added to counteract the reducing influence of liquid adulterants. Recently, too, guaiacum wood oil (so-called), an oil of fine odour which solidifies with a fine crystalline structure at ordinary temperatures, and consists of bodies much resembling those in oil of roses, has been used as an adulterant.

In this connection it may be mentioned that no standard for the quantity of stearoptene present in natural rose oil can be fixed, as climatic conditions appear to influence the ratio of the solid to the liquid portion very greatly. From 10 to 20 per cent. occurs in Bulgarian oil, whereas that obtained in the south of France, in England and in Germany has been stated to contain from 25 to 65 per cent. of stearoptene. In the case of so high a content as the latter figure, it is certain that the oil was not prepared in the normal way, probably being the result of distillation for rose water, very large quantities of water being used. Further, steam distilleries are being erected, and so far as one can judge at the present moment, an otto of different properties is obtained when distilled by steam instead of in the usual manner.

Oil of roses is not an easy oil to form an opinion upon with any degree of certainty. Gross adulterations can easily be detected, but judicious admixtures are less easy to deal with. Normally distilled Bulgarian otto has a specific gravity 0.850 to 0.860, rarely falling to 0.848 at  $\frac{30^{\circ}}{15^{\circ}}$ . The refractive index is a valuable

figure to determine, and should fall between 1.4580 and 1.4655.

## P E R F U M E R Y

Geraniol raises this figure perceptibly. Simmons gives 187 to 194 as the iodine absorption value for pure Bulgarian otto of rose. The oil is nearly inactive optically, and  $\pm 1^\circ$  to  $-- 4^\circ$  may be regarded as safe limits. The limits for the congealing point for the pure Bulgarian oil may be taken as from  $19^\circ$  to  $23^\circ$ , usually about  $20^\circ$  to  $21^\circ$ , but oils from other districts frequently have a higher congealing point than this.

Spermaceti or stearin is easily detected, whilst paraffin wax or the solid constituent of guaiacum wood oil (which is of an alcoholic nature) are not so easy of detection. As the stearoptene of pure rose oil consists of hydrocarbons, no fatty acids will be obtained by saponification, whereas spermaceti and stearin will yield, on saponification and decomposition of the resulting salts with hydrochloric acid, palmitic and stearic acids respectively, which may be identified by their melting points (palmitic acid from  $55^\circ$  to  $62^\circ$ , and stearic acid from  $62^\circ$  to  $68^\circ$ ). Paraffin will be indicated by the more granular structure of its crystals than that of the normal stearoptene, whilst the solid portion of guaiacum wood oil consists chiefly of a solid alcohol and will yield an acetyl figure, which is not the case with the normal stearoptene.

The percentage of free alcohols in the oil usually varies from 70 to 75 per cent., estimated as geraniol, by acetylation. Geranium oil gives from 75 to 95 per cent., so that no definite information is necessarily yielded by this determination. Dietze (*Suddl. Apoth. Zeit.*, xxvii, 89, p. 835) strongly recommends the acid and ester values to be determined by titration and saponification with seminormal alcoholic potash. This gives the following figures (in percentages of potash):—

|                 | Acid. | Ester. | Saponification. |
|-----------------|-------|--------|-----------------|
| German rose oil | 0.21  | 0.65   | 0.86            |
| Bulgarian       | 0.12  | 0.80   | 0.92            |
| "               | 0.14  | 0.75   | 0.89            |
| French geranium | 0.68  | 4.79   | 5.47            |
| "               | 0.50  | 5.41   | 5.91            |
| African         | 0.75  | 4.56   | 5.31            |
| Spanish         | 0.98  | 7.19   | 8.17            |
| Indian          | 0.15  | 3.10   | 3.25            |

Whilst there is no doubt that the ester value of most geranium oils is higher than that of rose oil, the above figures are not

# PERFUMERY

*Stearoptene Determinations. Burgess's Table.*

| Solvent.             | Otto of rose. |           | Geranium oil. |           | 5 per cent. |           | 10 per cent. |           | 15 per cent. |           | Citronellol. |           | 5 per cent. |           | 10 per cent. |           | 15 per cent. |           |
|----------------------|---------------|-----------|---------------|-----------|-------------|-----------|--------------|-----------|--------------|-----------|--------------|-----------|-------------|-----------|--------------|-----------|--------------|-----------|
|                      | I.            | II.       | I.            | II.       | I.          | II.       | I.           | II.       | I.           | II.       | I.           | II.       | I.          | II.       | I.           | II.       | I.           | II.       |
|                      | Per cent.     | Per cent. | Per cent.     | Per cent. | Per cent.   | Per cent. | Per cent.    | Per cent. | Per cent.    | Per cent. | Per cent.    | Per cent. | Per cent.   | Per cent. | Per cent.    | Per cent. | Per cent.    | Per cent. |
| 75 per cent. alcohol | *16.4         | *14.2     | *5.26         | *5.28     | *10.64      | *10.54    | *16.22       | *15.64    | *4.50        | *4.46     | *9.84        | *9.78     | *13.94      | *14.36    |              |           |              |           |
| 85                   |               |           | 4.52          | 4.42      | 9.56        | 9.76      | 15.26        | 15.14     | 4.34         | 4.30      | 9.10         | 9.10      | 13.18       | 13.78     |              |           |              |           |
| 90                   | 15.04         | 14.74     | 4.26          | 4.16      |             |           | 13.72        | 13.76     | 3.68         | 3.74      | 8.92         | 8.96      | 13.00       | 13.72     |              |           |              |           |
| 94                   | 14.4          | 14.1      | 3.84          | 3.88      | 8.58        | 8.56      | 13.40        | 13.44     | 3.20         | 3.16      | 8.24         | 8.50      | 13.00       | 12.66     |              |           |              |           |
| Acetone              | 13.8          | 14.0      | 3.68          | 3.84      | 4.82        | 4.66      |              |           |              |           | 4.62         | 4.62      |             |           |              |           |              |           |
|                      |               |           |               |           | 1.88        | 2.02      |              |           |              |           | 2.14         | 2.00      |             |           |              |           |              |           |
|                      |               |           |               |           | 6.70        | 7.23      | 13.38        | 13.44     | 3.12         | 3.08      | 6.76         | 6.62      | 12.16       | 12.16     |              |           |              |           |

\* In all these cases the precipitate and filter paper were distinctly oily, showing imperfect solution of the eleoptene.

## PERFUMERY

'comprehensive enough, and the indications obtained would be of very little value in the case of admixtures of considerable quantities of geranium oil.

Burgess finds that for the estimation of the stearoptene 85 per cent. alcohol gives the most accurate results. He finds that 5 grams of the otto (in these experiments he also used 5 grams of a standard solution of stearoptene in geranium oil and in citronellol—see table) in 25 c.c. of the solvent—or, if a weaker alcohol be used, 50 c.c.—is the most suitable quantity for the determination. Solution is effected by means of heat, and the liquid is then cooled in ice for five or six hours. The stearoptene is then filtered off on a disc and paper over a filter pump and washed, once if 85 per cent. alcohol be used, twice if a weaker spirit be employed; the paper with the separated stearoptene is then dried *in vacuo* over sulphuric acid for twelve hours. It is not necessary to tare the filter paper, since the stearoptene can be removed in one cake from the paper and weighed on a watch glass.

The table on p. 654 shows the results obtained with the various solvents on otto of rose, and on standard solutions of stearoptene in geraniol and in citronellol. With acetone he found, in some cases a further separation of stearoptene took place, so that he has recorded the results in the form of the two weighings of the stearoptene where necessary.

The addition of geranium oil (Indian) or geraniol may cause a rise in the specific gravity sufficient to bring that of the oil outside the limits given above, but in moderate quantity may avoid detection in this way. The optical rotation will scarcely be affected, but the congeling point will be lowered, and if the original otto contained only a moderate quantity of stearoptene, this figure will be reduced below the minimum allowable for pure oils. An examination of the stearoptene thus, as mentioned above, becomes necessary. By addition of alcohol and freezing as here described, the stearoptene can be almost entirely separated on a filter pump and washed with alcohol, and finally dried. It should then melt between 32° and 37°, usually at 33° to 34°. Spermaceti and most samples of paraffin wax will cause this to be rather higher, as will also "guaiacum wood" oil if present in more than very small quantities. Salol and antipyrin have been found as solid adulterants.

Jeancard and Satie (*Bull. Soc. Chim.*, 1904, 934) give the following method for the determination of the stearoptene. Ten

## P E R F U M E R Y

grams of the otto are weighed into a beaker and 50 c.c. of acetone added. The liquid is cooled to  $-10^{\circ}$ , without shaking, and then filtered through a funnel kept in a refrigerating mixture. The precipitated stearoptene is washed several times with similarly cooled acetone, and dried on the tared filter paper *in vacuo* over sulphuric acid.

The estimation of the total alcohols by acetylation gives results which are of limited value only. As, however, these alcohols are, in the main, a mixture of geraniol and citronellol, a separation of the two alcohols is of considerable value so long as the greatest care is exercised in deciding what the relative proportions ought to be in a pure sample of the type examined. What this is is not always easy to decide. In Bulgarian otto of rose the citronellol will usually be found to be present to the extent of about 40 per cent. of the total alcohols as determined by the acetylation process.

The citronellol is approximately determined by formylation as follows. Ten cubic centimetres of the otto are heated for an hour on a sand bath in an ordinary acetylation flask with twice its volume of formic acid (of specific gravity 1.226). The contents of the flask are cooled and 100 c.c. of water added, and the mixture transferred to a separator. The oil is washed with water until the washings are neutral, and the esters determined exactly as in the acetylation process. The citronellol is then calculated from the formula--

$$\text{Citronellol} = \frac{0.156 \times x \times 100}{w - 0.028x}$$

where  $x$  is the number of cubic centimetres of normal alcoholic potash solution used up, and  $w$  is the weight in grams of the formylated oil. (But see "Alcohols, Determination of.")

Subject to the reservations indicated above as to methods of distillation, genuine Bulgarian otto of rose has the following characters :—

|   |                              |
|---|------------------------------|
| Specific gravity at $\frac{30^{\circ}}{15^{\circ}}$ . | 0.849–0.860                  |
| Optical rotation . . .                                | $-1^{\circ}$ to $+4^{\circ}$ |
| Refractive index at $30^{\circ}$ .                    | 1.4580–1.4655                |
| Melting point . . .                                   | $19^{\circ}$ – $24^{\circ}$  |
| • Total alcohols as geraniol                          | 70–75 per cent.              |
| Citronellol . . . . .                                 | 25–35 „                      |
| Stearoptene content . .                               | 15–25 „                      |

The fixing of standards for French otto of rose and the analy



## PERFUMERY

of samples of this otto present considerably more difficulties than is the case with Bulgarian otto of rose. In the sequel, therefore, the reservations in regard to methods of distillation must be remembered, and too great stress must not be laid on the figures which have been observed for authentic samples, as other equally authentic samples may well have values outside such limits. As indicated above, the old-fashioned normal French otto of rose was that distilled from the Rose de Mai (*Rosa centifolia*) as more or less a by-product in the manufacture of rose water. The attempts to utilise the various roses known as *roses de jardin*, although successful up to a point, have left the question of standard characters in a very confused condition. The principal reason for this is that the yields of otto from the different roses vary greatly amongst themselves, so that if the same amount of roses and the same amount of water are used in identical stills under identical conditions, and the amounts of otto yielded by two different kinds of roses are very different, the inevitable result follows that, where the yield has been very small and the amount of water used very large, almost the whole of the more soluble constituents of the otto will be found in the rose water, whilst the separated oil will be quite abnormal, containing only the highly insoluble constituents. On the other hand, with a high yield of otto there will be sufficient of the more soluble constituents to saturate the water and still leave an appreciable amount for the separated otto. For example, the writer (E. J. P.) has examined an authentic sample distilled from the Rose d'Hai under conditions which were arranged for yield of otto rather than for that of rose water. Its specific gravity at 30° was 0.880, it melted at 8°, and it contained 90 per cent. of total alcohols. A sample distilled from the same roses at Thiviers by Gattefossé had the following characters.—

|                         |                |
|-------------------------|----------------|
| Specific gravity at 30° | . 0.8195       |
| Total alcohols          | . 22 per cent. |
| Melting point .         | . 30°          |

This otto, although "pure," would not be accepted by any judge of otto of rose as a *genuine* sample in the ordinary sense. It had been distilled with so much water that nearly all the odorous alcohols had been dissolved in the water, leaving something not much better than stearoptene. The above example indicates the difficulty in judging French otto of rose, and it cannot be too much emphasised that the trained nose is the most valuable asset an expert has in judging this product.

## P E R F U M E R Y

The following figures represent a number of typical samples of French otto of rose that have been examined. Jeancard and Satic (*Bull. Soc. Chim.*, 1904, 934) distilled a sample from the sepals only, which they found to have the following characters :—

|  |                 |
|--|-----------------|
| Congealing point . . . . .             | °°              |
| Stearoptene . . . . .                  | 51.13 per cent. |
| Specific gravity . . . . .             | 0.8704 at 15°   |
| Optical rotation . . . . .             | — 41°           |
| Melting point of stearoptene . . . . . | 14°             |
| Acid value . . . . .                   | 6.12            |
| Ester value . . . . .                  | 16.28           |
| Total alcohols . . . . .               | 13.99 per cent. |
| Citronellol . . . . .                  | 13.56 „         |

The melting point of the stearoptene is noteworthy, as it is far lower than that of the stearoptene obtained from the rose petals. An oil distilled from the whole flowers by Jeancard and Satic, with cohobation of the distillation waters, and one distilled from the whole flowers without cohobation of the distillation waters (so that 1 part of rose flowers gave 1 part of rose water), gave the following results :—

|                            | With<br>cohobation. | Without<br>cohobation. |
|----------------------------|---------------------|------------------------|
| Specific gravity at 15°    | 0.879               |                        |
| Optical rotation . . . . . | — 3°                |                        |
| Total alcohols . . . . .   | 88.5 per cent.      | 32 per cent.           |
| Citronellol . . . . .      | 22.4                | 15.1                   |
| Congealing point . . . . . | 25.5°               | 25.9°                  |
| Stearoptene . . . . .      | 32.2 per cent.      | 55.88 per cent.        |

*Schimmel & Co.* give the following values for two samples of French otto of rose distilled from the rose d'Hai :—

|                            |              |          |
|----------------------------|--------------|----------|
| Specific gravity at 30°    | 0.8706       | 0.8653   |
| Optical rotation . . . . . | — 1° 26'     | — 3° 20' |
| Refractive index at 25°    | 1.46486      | 1.46159  |
| Melting point. . . . .     | 13°          | 18.6°    |
| Acid value . . . . .       | 1.8          | 1.8      |
| Ester value . . . . .      | 6.3          | 5.2      |
| Total alcohols . . . . .   | 91 per cent. | 91.8 per |

# PERFUMERY

|   | 1                        | 2                        | 3                       | 4                       | 5                                      | 6                 |
|---|--------------------------|--------------------------|-------------------------|-------------------------|--|-------------------|
|   | German oil, Miltitz 1900 | German oil, Miltitz 1900 | Bulgarian oil (Kazanka) | Bulgarian oil (Kazanka) | Oil from Philippopolis from our expert | Purchased         |
| Specific gravity                        | At 10°<br>0 8372         | At 40°<br>0 8304         | At 30°<br>0 8366        | —                       | —                                      | —                 |
| Specific gravity                        | At 30°<br>0 8138         | At 33°<br>0 8360         | At 25°<br>0 8598        | At 25°<br>0 8394        | At 25°<br>0 8634                       | At 25°<br>0 8614  |
| Rotatory power                          | At 30°<br>— 0 44'        | At 33°<br>— 0 52'        | At 30°<br>— 2 20'       | At 25°<br>— 2 43'       | At 25°<br>— 2° 58'                     | At 25°<br>— 2 36' |
| Congealing point                        | + 29 0'                  | + 30 0'                  | + 20 0'                 | + 20 4'                 | + 19 6'                                | + 20 4'           |
| Stearoptene content.                    | 23 50 per cent           | 39 97 per cent           | 18 62 per cent          | 18 83 per cent          | 18 49 per cent                         | 20 55 per cent    |
| Acid number                             | 23                       | 0                        | 0                       | 23                      | 0                                      | 0                 |
| Saponification number                   | 45                       | 104                      | 11 03                   | 70                      | 11.1                                   | 101               |
| Saponification number after acetylation | 188 7                    | 171 14                   | 216 0                   | 204 1                   | 214 7                                  | 211 0             |
| Saponification number after formylation | 59 21                    | 47 9                     | 92 9                    | 96 8                    | 104 0                                  | 100 6             |
| Calculated from these figures —         |                          |                          |                         |                         |  |                   |
| Total alcohols $C_{10}H_{18}O$          | 60 44 per cent           | 54 00 per cent           | 70 58 per cent          | 66 27 per cent          | 70 37 per cent                         | 68 93 per cent    |
| Citronellol in the formylation product  | 16 49                    | 13 34                    | 25 88                   | 26 96                   | 28 97                                  | 28 03             |

## P E R F U M E R Y

has a specific gravity 0.9567; optical rotation,  $-1^{\circ} 40'$ ; refractive index, 1.48614; and is soluble in 0.5 volume of 90 per cent. alcohol. It contains citral and other aldehydes.

**TAGETES, OILS OF.**—*Schimmel & Co. (Report, Nov., 1908, 141)* have distilled the fresh flowering heads, with their bracts, of *Tageles patula*, a native of Mexico belonging to the natural order *Compositae*. The oil has a golden yellow colour and an aromatic odour, recalling that of a mixture of fruit esters and terpenes. The dried inflorescences yielded a similar oil, as did the air-dried stem and leaves. The oils had the following characters:—

|   | Fresh flowers.   | Dried flowers. | Stems and leaves. |
|---|------------------|----------------|-------------------|
| Specific gravity . . . . .              | 0.8856           | 0.8925         | 0.9034            |
| Optical rotation . . . . .              | $-5^{\circ} 35'$ | $-9^{\circ}$   | $+1^{\circ} 15'$  |
| Refractive index . . . . .              | 1.4971           | 1.4994         | 1.4994            |
| Acid value . . . . .                    | 2                | 6.4            | 14                |
| Ester value . . . . .                   | 18.7             | 10.6           | 12.4              |
| Ester value after acetylation . . . . . | 74.3             | —              | —                 |

*tes anisata* is a plant met with in the prairies of the Argentine. The green plant (*La Parfumerie Moderne*, 1921, 2, 32) yields 0.7 to 0.8 per cent. of essential oil containing much anethol and resembling aniseed oil in odour. It has a specific gravity 0.986, refractive index 1.5432, and congeals at  $-6^{\circ}$ .

The oil distilled from *Tageles minuta* has been examined at the Imperial Institute (*Bulletin*, 1924, xxii., 3). It is stated that the plant, which is a troublesome weed, yields 0.5 per cent. of volatile oil, and it was desired to ascertain whether it would be of commercial value. The oil is rather dark brown in colour and has a characteristic but not very pleasant odour. The clear filtered oil was found to have the following constants:—

|  |  |
|--|--|
| Specific gravity at $15/15^{\circ}$ C. . . . . | 0.9369   |
| Optical rotation $\alpha_D$ . . . . .          | $+1.7^{\circ}$   |
| Refractive index $n_{D_{20}}$ . . . . .        | 1.496  |
| Acid value . . . . .                           | 1.5  |
| Ester value before acetylation . . . . .       | 44.5   |
| Ester value after acetylation . . . . .        | 116.5  |
| Solubility in 90 per cent. alcohol             | Soluble in 1.5 parts and less (at $15^{\circ}$ C.), becoming cloudy on further dilution. |

## PERFUMERY

The characteristic odour is largely due to the presence of carvone, linalol and an olefinic terpene, either myrcene or ocimene. Linalyl acetate is also probably present, together with small amounts of pungent-smelling phenols. Linalol and carvone, the only constituents likely to be of any commercial interest, were not present in sufficient quantity to be worth extraction.

**TALAUMA OVATA.**—This plant is one of the most highly odorous trees growing wild. It is known in Brazil as *Pinho de Breja*. It is a small tree, occurring in the Organ Mountains and in the province of Minas Geraes. Its flowers and fruit are so highly odorous that their perfume is easily detected for a long distance in the forests. It is identical with the tree described as *Talauma fragrantissima* by Hooker ("Icones plantarum," vol. iii., Figs. 208-212).

**TALC.**—Finely powdered talc is employed on a very extensive scale as the basis of toilet powders: such powders have to a considerable extent replaced the old-fashioned so-called violet powder. The name talc has been applied to various minerals of a foliated nature, such as mica and gypsum. Its name is derived from the Arabic *talq*. Steatite is the name reserved for the massive varieties of talc.

Talc is a hydrogen magnesium silicate of a greater or less degree of purity, and in its theoretically pure state has the composition indicated by the formula  $H_2Mg_3Si_4O_{12}$ . A typical analysis is as follows:—

|                                |   |   |   |             |   |              |
|--------------------------------|---|---|---|-------------|---|--------------|
| SiO <sub>2</sub>               | . | . | . | .           | . | 60 per cent. |
| Al <sub>2</sub> O <sub>3</sub> | . | . | . | .           | . | Traces.      |
| FeO                            | . | . | . | .           | . | Traces.      |
| MnO                            | . | . | . | (sometimes) | . | Traces.      |
| CaO                            | . | . | . | "           | . | 34 "         |
| MgO                            | . | . | . | .           | . | 6 "          |
| H <sub>2</sub> O               | . | . | . | .           | . | "            |

It is widely distributed, in very varying degrees of purity, and for toilet uses should be absolutely white. Samples containing more than mere traces of iron and manganese are green in colour and useless for this purpose.

It is found in Cornwall, in the Tyrolean Alps, the Pyrenees, Piedmont, and in numerous parts of the United States. The last-named country alone produces in the neighbourhood of 150,000 tons per annum.

Powdered talc is non-gritty, soft, and greasy to the touch. It is used, faintly perfumed, as "glove powder," but its principal

## P E R F U M E R Y

employment in perfumery is as a face powder, when it is coloured and perfumed to taste. It is often used alone, but is also used mixed with starch, especially maize starch.

**TANACETONE.**—See “Thujone.”

**TANACETUM OILS.**—The essential oils of three species of *Tanacetum* (natural order *Compositæ*) have been carefully examined. These are the following :—

*Tanacetum vulgare.*—This plant is widely distributed over most European countries. It is commonly known as tansy. Its essential oil is strongly aromatic. It is cultivated to a small extent in the United States. The fresh flowering herb yields from 0.1 to 0.2 per cent. of essential oil, but the characters vary somewhat according to the locality of growth. The oil usually has characters falling within the following limits :—

|                               |           |                |
|-------------------------------|-----------|----------------|
| Specific gravity              | . . . . . | 0.925–0.936    |
| Optical rotation              | . . . . . | – 27° to + 34° |
| Refractive index              | . . . . . | 1.4570 1.4595  |
| Acid value                    | . . . . . | 1–2            |
| Ester value                   | . . . . . | 10–35          |
| Ester value after acetylation | . . . . . | 28 80          |

English-distilled oil, which is not now a commercial article, has an odour resembling that of rosemary, and is highly levorotatory. The oil consists mainly of thujone (tanacetone) (*q.v.*), and also contains the alcohol borneol.

*Tanacetum Boreale.*—The half-dried herb *Tanacetum boreale*, a plant found in Siberia, yielded on distillation, 0.12 per cent. of an essential oil which had a powerful odour of thujone. It had a specific gravity 0.9218, and an optical rotation + 48° 25'.

The oil obtained from the fresh herb was viscid and of a greenish-brown colour. It had a specific gravity 0.9603; refractive index, 1.49167; acid value, 30.5; and ester value, 40.6. (*Vide Schimmel's Report*, October, 1904, 97; 1905, 66.)

*Tanacetum Balsamita.*—*Schimmel & Co.* (*Report*, Oct., 1897, 60) obtained 0.064 per cent. of essential oil on distillation of the fresh flowering herb *Tanacetum balsamita*. The odour was agreeably balsamic, resembling that of ordinary tansy. It had a specific gravity 0.943, optical rotation – 43° 40' to – 53° 48', and acid value 21. The oil distilled between 207° and 283°.

**TARRAGON OIL.**—Tarragon or estragen oil is the distillate from the flowering herb *Artemisia Dracunculus* (natural order *Compositæ*). It is used both in conserves and in the prepara-

## P E R F U M E R Y

tion of toilet vinegars. The yield from the dried herb is from 0.25 to 0.8 per cent. Tarragon oil is colourless to pale green and of a sweet odour resembling that of aniseed. It consists mainly of methyl-chavicol ("estragol"). It also contains an aliphatic terpene, phellandrene, and a little *para*-methoxy-cinnamic acid. The oil usually has the following characters —

|                               |       |               |
|-------------------------------|-------|---------------|
| Specific gravity              | . . . | 0.900–0.947   |
| Optical rotation              | . . . | + 2° to + 10° |
| Refractive index              | . . . | 1.5020–1.5160 |
| Acid value                    | . . . | 0–2           |
| Ester value                   | . . . | 1–10          |
| Ester value after acetylation |       | 15            |

An oil distilled by *Roure-Bertrand Fils* (*Bulletin*, October, 1910, 43) had somewhat different characters from the above. The specific gravity was 0.9814; optical rotation, + 2° 56'; and saponification value, 29.8.

**TASMANOL.**—Tasmanol is a liquid phenol, colourless when freshly prepared, but darkening on keeping, which was isolated from the essential oil of *Eucalyptus linearis* by Robinson and Smith (*Jour. Proc. Roy. Soc. N.S.W.*, 1914, 48, 518). It has an aromatic odour recalling that of carvacrol, and has the following characters :—

|                         |       |           |
|-------------------------|-------|-----------|
| Specific gravity at 23° | . . . | 1.077     |
| Refractive index at 22° | . . . | 1.5269    |
| Optical rotation        | . . . | 0°        |
| Boiling point           | . . . | 268°–273° |

**TAXODIUM, OIL OF.**—The wood of the southern cypress, *Taxodium distichum*, yields an essential oil, which has been examined by Odell (*Jour. Amer. Chem. Soc.*, 33, 755). In it he found a sesquiterpene, which he termed cypressene, and an aldehyde,  $C_{12}H_{20}O$ , to which he gave the name cypral. This is a highly odorous oil, boiling at 182° to 185° at 35 mm.

**TCHOW-LANG-RHOA.**—This is the Chinese name for *Chloranthus inconspicus*, the name signifying "the pearl of flowers." The plant is a shrub with long spikes of elegant white blossom of very delicate perfume. It is cultivated especially in the provinces of Ngan-Houi and So-Tchowán, and the dried flowers are much used for perfuming tea and generally in Chinese perfumery.

**TCHOW-MEI.**—This climbing plant, *Actinidia chinensis*, is plentiful in the Yang-tse valley, and is much esteemed in China

## PERFUMERY

as a perfume plant, its large yellow flowers being very odorous. It is known to Europeans as the Itchang currant.

**TEA, OIL OF.**—The essential oil of dried tea leaves (from *Thea chinensis*) was obtained by van Romburgh to the extent of 0.006 per cent. (*Verslag Plantentuin te Buitenzorg*, 1895, 119; 1896, 166). The oil appears to be the result of fermentation of the leaves during drying, probably through the action of an enzyme on a glucoside. The oil had a specific gravity 0.866 at 26°, and an optical rotation of about  $-0^{\circ} 5'$ . Its principal constituent is an alcohol of the formula  $C_6H_{12}O$ . It also contains methyl salicylate. From the young leaves of *Thea Sasangua*, a Japanese plant, Kimura (*Berichte d. deutsch. pharm. Gesell.*, 1911, 21, 209) obtained from 0.4 to 1 per cent. of an essential oil with a sweetish odour. It had a specific gravity 1.0611 at 21°, and was optically inactive. It contained about 97 per cent. of eugenol, and possibly traces of a geraniol ester, and an aldehyde or ketone.

**TEMU-KUNTJI.**—In Java, the rhizomes of *Gastrochilus pandurata* are known as *temu-kuntji*. On distillation they yield from 0.1 to 0.37 per cent. of an essential oil resembling tarragon and basil oils. It has a specific gravity 0.8746; optical rotation,  $-10^{\circ} 24'$ ; refractive index, 1.4896; acid value, 0; and ester value, 17.3.

**TERESANTALOL.**—This body is one of the alcohols occurring in small amount in oil of sandalwood. It has the formula  $C_{10}H_{16}O$ , and has been artificially prepared by Semmler and Bartelt (*Berichte*, 1907, 3321) by the reduction of teresantallic acid by means of sodium. It forms fine prismatic crystals melting at 112° to 114°. It forms a phthalic acid compound melting at 140°.

**TERPENELESS OILS.**—A great many essential oils contain more or less of hydrocarbon constituents, which are of practically no value as odour bearers, and which form the least soluble portion of the oil. By the removal of these hydrocarbons a concentrated oil is obtained, and, further, the portion which is least soluble in diluted alcohol is removed, so that in actual practice a considerable economy in alcohol is effected.

In the main, terpeneless oils are considered sufficiently deprived of their insoluble constituents for ordinary use, but in a certain number of cases it is considered advisable to remove the sesquiterpenes as well. Oils from which the terpenes only have been



## P E R F U M E R Y

removed are usually designated T.F. commercially (terpene free), and those from which both the terpenes and the sesquiterpenes have been removed are designated S.T.F. (sesquiterpene and terpene free).

These concentrated oils are usually prepared by fractional distillation under greatly reduced pressure. In rare cases a few oils are prepared by a "cold process" of extraction of the oxygenated constituents by means of dilute alcohol, and subsequent recovery of the alcohol, but they are generally manufactured by distillation. (*Vide* "Distillation.")

The principal oil which is rendered terpeneless is lemon oil, and the characters and examination of this oil will be found dealt with under "Lemon Oil."

The table on p. 732 summarises the characters of the principal terpeneless oils (*Perfumery and Essential Oil Record Year Book and Diary* for 1924).

Sachsse & Co. (*P. & E. O. R.*, 1911, 12) give the following figures for a few of the less common oils which have been rendered free from terpenes and sesquiterpenes. In the table the characters of the natural oil are compared with the S.T.F. oil, and the following abbreviations are used:—

S.G. = specific gravity at 15° C., unless otherwise indicated.  
O.R. = optical rotation. Sol. 21·8 o. = solubility in alcohol of 21·8 over proof, and so forth. Sol. 11·5 u. = solubility in alcohol of 11·5 under proof. S.V. = saponification value. S.V.A.O. = saponification value of the acetylated oil.

### *Angelica Oil from Roots*

| Natural oil. |                  | S.T.F. oil.    |                 |
|--------------|------------------|----------------|-----------------|
| S.G. . . .   | 0·8565–0·910     | S.G. . . .     | 0·975–0·988     |
| O.R. . . .   | + 15° to + 31°   | O.R. . . .     | Slightly + to — |
| Sol. 58 o. . | Mostly insoluble | Sol. 21·8 o. . | 1 : 2·5–4       |
| S.V. . . .   | 15–22            | S.V. . . .     | 75–95           |
| S.V.A.O. . . | 30–40            | S.V.A.O. . .   | 200–230         |

### *Bay Leaf Oil*

| Natural oil. |                  | S.T.F. oil.    |                        |
|--------------|------------------|----------------|------------------------|
| S.G. . . .   | 0·965–0·980      | S.G. . . .     | 1·030–1·045            |
| O.R. . . .   | Up to – 2°       | O.R. . . .     | Nearly always inactive |
| Sol. 58 o. . | Mostly insoluble | Sol. 21·8 o. . | 1 : 1·2–1·5            |
| Phenol cont. | 50–65 per cent.  | Sol. 5·9 o. .  | 1 : 4–6                |
|              |                  | Sol. 11·5 u. . | 1 : 75–100             |
|              |                  | Phenol cont.   | 65–85 per cent.        |

# PERFUMERY

## Patchouli Oil

| Natural oil. |                  | S.T.F. oil.  |                      |
|--------------|------------------|--------------|----------------------|
| S.G.         | 0.970-0.985      | S.G.         | Slightly more than 1 |
| O.R.         | - 50° to - 68°   | O.R.         | - 60° to - 78°       |
| Sol. 58 o.   | 1 : 1-1.5 to 1-8 | Sol. 21.8 o. | 1 : 5                |
| S.V.         | 5-10             | S.V.         | 15-30                |
| S.V.A.O.     | 20-45            | S.V.A.O.     | 65-90                |

## Pine Oil (*Abies Pectinata*)

| Natural oil.  |                | S.T.F. oil.   |                 |
|---------------|----------------|---------------|-----------------|
| S.G.          | 0.868-0.875    | S.G.          | 0.956-0.970     |
| O.R.          | - 20° to - 60° | O.R.          | - 20° to - 30°  |
| Sol. 58 o.    | 1 : 5-8        | Sol. 21.8 o.  | 1 : 4           |
| Bornylacetate |                | Sol. 5.9 o.   | 1 : 30          |
| content       | 4-7 per cent.  | Sol. 11.5 u.  | 1 : 175         |
|               |                | Bornylacetate |                 |
|               |                | content       | 45-60 per cent. |

## Pine Oil (*Pinus Pumilio*)

| Natural oil.  |               | S.T.F. oil.   |                 |
|---------------|---------------|---------------|-----------------|
| S.G.          | 0.865-0.875   | S.G.          | 0.940-0.955     |
| O.R.          | - 4° to - 10° | O.R.          | - 15° to - 25°  |
| Sol. 67 o.    | 1 : 1.5-2.5   | Sol. 21.8 o.  | 1 : 2.5         |
| Bornylacetate |               | Sol. 5.9 o.   | 1 : 25          |
| content       | 4-7 per cent. | Sol. 11.5 u.  | 1 : 150         |
|               |               | Bornylacetate |                 |
|               |               | content       | 40-55 per cent. |

## Pine Oil (*Pinus Sibirica*)

| Natural oil.  |                 | S.T.F. oil.   |                 |
|---------------|-----------------|---------------|-----------------|
| S.G.          | 0.904-0.918     | S.G.          | 0.979-0.986     |
| O.R.          | - 39° to - 42°  | O.R.          | - 36° to - 40°  |
| Sol. 58 o.    | 1 : 1-1.5       | Sol. 21.8 o.  | 1 : 3           |
| Bornylacetate |                 | Sol. 5.9 o.   | 1 : 13          |
| content       | 27-35 per cent. | Sol. 11.5 u.  | 1 : 100         |
|               |                 | Bornylacetate |                 |
|               |                 | content       | 80-90 per cent. |

## Ylang-Ylang Oil (*Manila*)

| Natural oil. |                | S.T.F. oil. |                |
|--------------|----------------|-------------|----------------|
| S.G.         | 0.930-0.950    | S.G.        | 0.950-0.967    |
| O.R.         | - 38° to - 50° | O.R.        | - 22° to - 40° |
| Sol. 67 o.   | Insoluble      | Sol. 41 o.  | 1 : 1.5        |
| S.V.         | 80-100         | S.V.        | 130-150        |
| S.V.A.O.     | 110-140        | S.V.A.O.    | 160-200        |

## P E R F U M E R Y

E. J. Parry (*La Parfumerie Moderne*, 1923, 101) gives the following figures for commercial lemon and orange oils —

### *Terpeneless Lemon Oils*

|                  | 1           | 2           | 3           | 4           | 5           | 6           |
|------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Specific gravity | 0.895       | 0.893       | 0.892       | 0.888       | 0.891       | 0.893       |
| Optical rotation | -5° 30'     | +0°         | -3° 30'     | +6°         | -5°         | 6°          |
| Refractive index | 1.4800      | 1.4810      | 1.4801      | 1.4770      | 1.4792      | 1.4810      |
| Citral content   | 46 per cent | 42 per cent | 43 per cent | 39 per cent | 42 per cent | 41 per cent |

One expects a definite levorotation in terpeneless lemon oils. Samples Nos. 2 and 4 were further examined, and in the case of No. 2 distinct traces of terpenes were detected. In the case of No. 4, 5 per cent of alcohol was found to be present as well as heavy traces of terpenes, so that both samples were considered unsatisfactory, the latter especially.

### *Terpeneless Orange Oils*

|                  | 1      | 2        | 3      | 4        | 5      |
|------------------|--------|----------|--------|----------|--------|
| Specific gravity | 0.876  | 0.866    | 0.878  | 0.858    | 0.878  |
| Optical rotation | +27°   | +17° 20' | +30°   | +87° 30' | +26°   |
| Refractive index | 1.4643 | 1.4660   | 1.4740 | 1.4730   | 1.4640 |

Sample No. 2 was found to contain 10 per cent of alcohol, and sample No. 4 was merely a slightly concentrated oil containing an enormous amount of terpenes.

### *Sesquiterpeneless Lemon Oils*

|                  | 1           | 2           | 3           | 4           |
|------------------|-------------|-------------|-------------|-------------|
| Specific gravity | 0.898       | 0.8995      | 0.900       | 0.8979      |
| Optical rotation | 5°          | -5° 30'     | -4°         | -1° 30'     |
| Refractive index | 1.4830      | 1.4820      | 1.4822      | 1.4792      |
| Citral           | 63 per cent | 64 per cent | 62 per cent | 61 per cent |

None of these samples showed any appreciable hydrocarbon residues.

# PERFUMERY

## Sesquiterpeneless Orange Oils

|                  | 2.        | 3.        | 4.     |
|------------------|-----------|-----------|--------|
| Specific gravity | 0.858     | 0.885     | 0.888  |
| Optical rotation | + 68° 30' | + 15° 30' | + 17°  |
| Refractive index | 1.4720    | 1.4765    | 1.4780 |
|                  |           |           | 1.4495 |

Sample No. 1 was merely a slightly concentrated oil rich in hydrocarbons. Sample No. 4 is most extraordinary.

Its low refractive index is conclusive against it being a genuine oil. Alcohol was absent, and hydrocarbons were substantially absent. The characters of this oil would be accounted for by the addition of such synthetic bodies as decyclic aldehyde, and this sample was adulterated with some form of synthetic orange oil.

**TERPENES.**—The terpenes consist of a number of isomeric substances of the most varied constitution, of the general formula  $C_{10}H_{16}$ . From the perfumery point of view, they are of very little value, and in most cases rather objectionable than otherwise. Their importance to the perfumer lies in the desirability of getting rid of them. In the first place, their odour is either very slight or is of no perfume value. It is true that where essential oils contain so much terpene that it is a common practice to remove them, and so produce terpeneless oils (*q.v.*), the terpenes so removed always contain a small amount of the more highly odorous compounds of the oil (which almost invariably contain oxygen), so that they have a slight perfume value. Such terpene mixtures, however, only find employment in the cheapest of perfume industries, such as common soap, blacking, and other household articles.

The second objection to the terpenes is that they are far less soluble in alcohol than the oxygenated constituents of the oil, and by their removal, when present in appreciable quantities, a considerable saving in alcohol and in troublesome filtration is effected.

The third objection to these bodies is that many of them are very easily oxidised or otherwise altered by exposure to air, light, and moisture, and develop objectionable odours. So much is this the case that many oils very rich in terpenes cannot be kept beyond a certain time in a fit state for use, whereas many others, almost or quite free from terpenes, can be kept for prolonged periods with advantage to their odour value.

\* The constitution of the terpenes was for many years a baffling mystery. Although excellent work was done by numerous chemists, both British and foreign, it is to Otto Wallach that credit must be given for attacking the problems to be solved in a laborious and systematic method. Then followed a period when numerous chemists, mostly German, fascinated by the success attending Wallach's researches, devoted themselves to this branch of organic chemistry. It is, however, the extraordinary researches of W. H. Perkin, jun. (the son of W. H. Perkin who discovered the first coal-tar dye), and his pupils, which resulted, *inter alia*, in the syntheses of dipentene and sylvestrene, that have brought our knowledge of these bodies nearer to a state of certainty than any other chemical investigations whatever.

For details of the pure chemistry of the terpenes, chemical literature (*passim*) must be consulted. For a short summary of the properties, "The Chemistry of Essential Oils," vol. ii. (E. J. Parry; Scott, Greenwood & Co) and "The Volatile Oils" (Gildemeister and Hoffmann; Schimmel & Co) may be consulted.

Whilst the terpenes properly so called are ring or closed-chain compounds, there are a few bodies of the same empirical formula,  $C_{10}H_{16}$ , which are sufficiently similar in some of their properties to the terpenes to have been called "olefinic terpenes." Of these, however, only a comparatively small number are known.

Apart from the proper nomenclature of the terpenes from a purely constitutional point of view, which is based on hexahydro-*para*-cymene, or *para*-menthane as it is usually called, an objectionable practice has grown up in naming terpenes in such a manner that the names give no possible indications of chemical relationship; indeed, often the contrary is achieved, and chemical relationships indicated which do not exist. For example, there are four "pinenes" known. These are termed  $\alpha$ -pinene,  $\beta$ -pinene,  $\delta$ -pinene, and *iso*-pinene. Each one of these has an entirely different constitution, and, except for some trivial reasons of convenience, there is no justification for calling them "pinene" in any case. Similar confusion exists in the case of the fenchenes and the phellandrenes.

It is to be hoped that at no distant date an agreement as to nomenclature may be reached by which it will be possible to avoid the chaotic conditions at present existing.

Amongst the most important of the terpenes, the following may be shortly described:—

**$\alpha$ -Pinene.**—This is the most commonly occurring terpene,

## P E R F U M E R Y

constituting in its dextrorotatory form the bulk of American and several other varieties of turpentine oil. In its laevorotatory form it is present in French oil of turpentine, and, to a greater or less extent, is found in many hundreds of essential oils. The purest specimens of the three optical isomers that have been prepared have the following characters —

|                       | Dextrorotatory. | Laevorotatory | Inactive. |
|-----------------------|-----------------|---------------|-----------|
| Boiling point . . .   | 155°–156°       | 155°–156°     | 155°–156° |
| Specific gravity . .  | 0.864           | 0.865         | 0.862     |
| Refractive index . .  | 1.4656          | —             | 1.4655    |
| Specific rotation . . | + 48.4°         | — 48.6°       | ± 0°      |

**β-Pinene.**—This terpene, more properly known as nopinene, is found in oil of hyssop, and in most turpentine oils in association with α pinene, as well as in small amount in numerous other essential oils. It has also been prepared artificially by Wallach (*Annalen*, 245, 251). Its characters are approximately as follows —

|                  |        |
|------------------|--------|
| Boiling point    | 164°   |
| Specific gravity | 0.866  |
| Optical rotation | — 20°  |
| Refractive index | 1.4740 |

According to Varon (*Comptes Rendus*, 1909, 149, 997), the following are the approximate quantities of α pinene and β pinene in French, American, and German turpentine oils —

|                  | α P nene    | β P nene     |
|------------------|-------------|--------------|
| French oil . . . | 63 per cent | 37 per cent. |
| American oil . . | 73          | 27 „         |
| German oil . . . | 72 „        | 28 „         |

**Iso-Pinene.**— See Aschan (*Berichte*, 1909, 40, 997).

**Camphene.**—Camphene is the only well recognised natural terpene which is crystalline. It has the following characters —

|                        |                        |
|------------------------|------------------------|
| Melting point . . .    | 50°–52°                |
| Boiling point . . .    | 159°–161°              |
| Specific rotation . .  | —                      |
| Refractive index . . . | 1.4550 (liquid at 50°) |
| Specific gravity . . . | 0.856 at 40°           |

It is prepared artificially by converting pinene into pinene hydrochloride, and then withdrawing the hydrochloric acid, when

## P E R F U M E R Y

camphene results from a molecular rearrangement. This terpen is of particular importance, as it is an intermediate in the manufacture of artificial camphor from turpentine.

**Dipentene.**—Dipentene, or more correctly inactive limonene, is a terpene occurring to a considerable extent in nature. In the form of limonene, principally *dextro*-limonene, it forms the greater part of several of the *Citrus* oils, especially orange and lemon. It also occurs to a considerable extent in dill and caraway oils. The terpene has the following characters:—

|                            |                  |
|----------------------------|------------------|
| Boiling point . . . . .    | 175°–176°        |
| Specific gravity . . . . . | 0·848 0·850      |
| Refractive index . . . . . | 1·4745           |
| Optical rotation . . . . . | + 105° or – 105° |

For the classic synthesis of this terpene by W. H. Perkin and his pupils, see the following: W. H. Perkin, Lecture to the Pharmaceutical Society, May, 1912 *Jour. Chem. Soc.*, 1904, **85**, 416, 654.

**Sylvestrene.**—Sylvestrene is a terpene found to a considerable extent in Swedish and other turpentine oils. As is the case with limonene, the inactive variety, which is properly termed *i*-sylvestrene, is commonly termed carvestrene.

The purest specimens of natural sylvestrene so far prepared (and which are always dextrorotatory) had the following characters —

|                            |                |
|----------------------------|----------------|
| Boiling point. . . . .     | 176°–180°      |
| Specific gravity . . . . . | 0·851          |
| Refractive index . . . . . | 1·4757–1·4779  |
| Optical rotation . . . . . | + 60° to + 80° |

It is, however, possible that the sylvestrene isolated from Swedish turpentine oil is a mixture of more than one terpene.

Sylvestrene has been completely synthesised by W. H. Perkin and his pupils.

**Phellandrene.**—There are two isomeric terpenes known as phellandrene,  $\alpha$ -phellandrene and  $\beta$ -phellandrene. They are found in a number of essential oils, especially eucalyptus oils and water fennel oil. The purest specimens yet isolated had the characters shown on p 710.

Wallach has prepared  $\alpha$ -phellandrene synthetically (*Annalen*, **359**, 265).

**Terpinene.**—Three terpenes are known as terpinene:  $\alpha$ -terpinene,  $\beta$ -terpinene, and  $\gamma$ -terpinene. Only the first and the last have been found in nature. The chemistry of these terpenes is

## P E R F U M E R Y

not well understood, but Semmler (*Berichte*, 1908, 41, 4474; 1909, 42, 522) has done much to elucidate their constitutions.

|                  | <i>dextro</i> -<br>$\alpha$ -Phellandrene. | <i>dextro</i> - $\beta$ -<br>Phellandrene. | <i>laevo</i> - $\alpha$ -<br>Phellandrene. |
|------------------|--|--|--|
| Specific gravity | 0.844 at 19°                               | 0.852 at 20°                               | 0.848 at 15°                               |
| Boiling point    | 175°                                       | —  | 174°                                       |
| Refractive index | 1.4732                                     | 1.4788                                     | 1.4769                                     |
| Optical rotation | + 40° 40'                                  | + 14° 45' to<br>+ 18° 30'                  | — 84° 10'                                  |

**Terpinolene.**—This terpene is rarely met with in nature, but forms a considerable proportion of the residues from terpineol manufacture. The commercial "terpinolene" is principally such residues containing a substantial quantity of the terpene. *Pure* terpinolene has the following characters:—

|                         |           |
|-------------------------|-----------|
| Specific gravity at 20° | 0.854     |
| Refractive index        | 1.4840    |
| Boiling point           | 183°–185° |
| Optical rotation        | ± 0°      |

For further details of the above and other terpenes, the general literature indicated above should be referred to.

The only two so-called olefinic terpenes that are commonly found in any essential oils are myrcene and ocimene. The former is present in oil of bay, West Indian lemongrass oil, and a few others, whilst the latter is present in certain types of basil oil. The characters of these olefinic terpenes are different from those of the terpenes proper, the specific gravity, especially, being much lower. The two bodies mentioned have the following characters:—

|                  | Myrcene. |    | Ocimene. |
|------------------|----------|----|----------|
| Specific gravity | 0.801    | .. | 0.803    |
| Refractive index | 1.4700   | .. | 1.4850   |
| Boiling point    | 167°     | .. | 172°     |

**TERPINENOL.**—This alcohol, of the formula  $C_{10}H_{18}O$ , is present in the essential oils of marjoram, cardamom, juniper, cypress, and nutmeg. It is prepared artificially by treating sabinene or thujene with dilute sulphuric acid. It is doubtful if it has been isolated in a pure condition, but Wallach (*Annalen*, 1907, 356, 215) gives the following as its characters:—

|                         |           |
|-------------------------|-----------|
| Boiling point           | 209°–212° |
| Specific gravity at 19° | 0.9265    |
| Refractive index at 19° | 1.4785    |
| Optical rotation        | + 25° 4'  |



## P E R F U M E R Y .

**TERPINEOL.**—This substance is one of the most valuable, and one of the most largely employed of the cheaper artificial perfumes. It is used in all perfumes of the lilac and lily of the valley types, and is employed on a large scale in soap perfumery, not only on account of its low price, but also because it is very stable towards both heat and free alkali. There are a large number of isomeric terpineols, of which several have been prepared artificially, and one or more found naturally in a few essential oils. Commercial terpineol is a mixture of at least two, or possibly three, of these isomers.

Although the greater part of commercial terpineol probably consists of crystalline bodies melting at over  $30^{\circ}$ , the mixture—containing impurities, such as, probably, a third isomeric liquid terpineol—is a liquid which does not crystallise. The purified isomers are not commercial articles, and need not be described here, as they have no interest at all to perfumers. A properly prepared commercial terpineol should have the following characters —

|                            |   |
|----------------------------|---|
| Specific gravity . . . . . | 0.933–0.941                                     |
| Boiling point . . . . .    | $217^{\circ}$ – $220^{\circ}$                   |
| Refractive index . . . . . | 1.4800–1.4840                                   |
| Optical rotation . . . . . | Not more than<br>+ $2^{\circ}$ to – $2^{\circ}$ |

Naturally-occurring terpineol is always highly optically active, up to +  $100^{\circ}$  or –  $100^{\circ}$ .

Fuller and Kenyon (*Jour. Chem. Soc.*, 1924, 2304) have described a method for the resolution of  $\alpha$  terpineol into its optically active varieties. This method depends on the fractional crystallisation of the brucine and morphine salts of the hydrogen phthalate esters of the terpineol. The optical activity of  $\alpha$  terpineol has proved to be  $\pm 100.5^{\circ}$  —

The isomers constituting the bulk of artificial commercial terpineol are  $\alpha$ -terpineol and  $\beta$ -terpineol, which, in a pure condition, have the following characters. —

|                  | $\alpha$ Terpineol            |    | $\beta$ Terpineol.          |
|------------------|-------------------------------|----|-----------------------------|
| Melting point    | $35^{\circ}$                  | .. | $32^{\circ}$ – $33^{\circ}$ |
| Boiling point.   | $217^{\circ}$ – $218^{\circ}$ | .. | $210^{\circ}$               |
| Refractive index | 1.4808                        | .. | 1.4747                      |
| Specific gravity | 0.935–0.940                   | .. | 0.923                       |

Terpineol is manufactured from turpentine oil as the starting point. The first part of the process is the hydration of the terpenes with formation of terpin hydrate. One hundred and fifty litres

## P E R F U M E R Y

not well understood, but Semmler (*Berichte*, 1908, 41, 4474; 1909, 42, 522) has done much to elucidate their constitutions.

|                  | <i>dextro</i> -<br>α Phellandrene. | <i>dextro</i> β<br>Phellandrene. | <i>laevo</i> -α-<br>Phellandrene. |
|------------------|------------------------------------|----------------------------------|-----------------------------------|
| Specific gravity | 0.844 at 19°                       | 0.852 at 20°                     | 0.848 at 15°                      |
| Boiling point    | 175°                               | —                                | 174°                              |
| Refractive index | 1.4732                             | 1.4788                           | 1.4769                            |
| Optical rotation | + 40° 40'                          | + 14° 45' to<br>+ 18° 30'        | — 84° 10'                         |

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|------------------|---------|----|----------|
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|                         |           |
|-------------------------|-----------|
| Boiling point           | 209°–212° |
| Specific gravity at 19° | 0.9265    |
| Refractive index at 19° | 1.4785    |
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## P E R F U M E R Y

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|                            |   |
|----------------------------|---|
| Specific gravity . . . .   | 0.933–0.941                                     |
| Boiling point . . . . .    | $217^{\circ}$ – $220^{\circ}$                   |
| Refractive index . . . . . | 1.4800–1.4840                                   |
| Optical rotation . . . . . | Not more than<br>+ $2^{\circ}$ to – $2^{\circ}$ |

Naturally-occurring terpineol is always highly optically active, up to +  $100^{\circ}$  or –  $100^{\circ}$ .

Fuller and Kenyon (*Jour Chem Soc*, 1924, 2304) have described a method for the resolution of  $\alpha$  terpineol into its optically active varieties. This method depends on the fractional crystallisation of the brucine and morphine salts of the hydrogen plithic esters of the terpineol. The optical activity of  $\alpha$  terpineol has proved to be  $\pm 100.5^{\circ}$ .

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|                            | $\alpha$ Terpineol            |    | $\beta$ Terpineol.          |
|----------------------------|-------------------------------|----|-----------------------------|
| Melting point              | $35^{\circ}$                  | .. | $32^{\circ}$ – $33^{\circ}$ |
| Boiling point. . . . .     | $217^{\circ}$ – $218^{\circ}$ | .. | $210^{\circ}$               |
| Refractive index . . . . . | 1.4808                        | .. | 1.4747                      |
| Specific gravity . . . . . | 0.935–0.940                   | .. | 0.923                       |

Terpineol is manufactured from turpentine oil as the starting point. The first part of the process is the hydration of the terpenes with formation of terpin hydrate. One hundred and fifty litres

## PERFUMERY

of oil of turpentine and 100 litres of nitric acid (specific gravity 17 to 21 Baumé) are mixed in a stoneware vessel, the specific gravity of the acid being chosen according to the temperature—higher in cold weather and lower in hot weather. The mixture is agitated by a wooden stirrer, preferably made of pitch pine, which resists the action of the acid better than any other wood. The temperature should not be allowed to rise, and the extreme temperature when acid of 17° is used should be 30° C, or when acid of 21° is used 25° C. If nitrous fumes are evolved, it means that the temperature is too high, and the yield will be low. The separated turpin with unaltered turpentine is rendered alkaline with sodium carbonate, and the unaltered turpentine distilled off. The turpin hydrate is washed with water to remove excess of alkali, when it should form brilliant prismatic crystals melting at 116°. It is optically inactive. It is now dehydrated by means of a suitable acid, phosphoric acid being the best for the purpose. It should be used in the proportion of 2 to 3 per 1,000, and the mixture boiled, when crude terpineol results, which is purified by distillation. The residues after this distillation, contain a certain amount of terpineol, together with numerous other more or less odorous substances not identified. This residue is sold under the name 'terpinolene' (it is not to be confused with the *terpene* of this name) and is used in the very cheapest soaps as a perfume, or for perfuming boot blacking and similar inexpensive products.

Bubier and Gignard (*Comptes Rendus*, 1907, 145, 1425) recommend the following method for the preparation of terpineol. One kilogram of pinene, 1 kg of glacial acetic acid, 100 c.c. of acetic anhydride, and 100 c.c. of a 50 per cent solution of benzene mono sulphonic acid are mixed. The temperature rises to about 70°. In two hours the oily liquid is washed with water and distilled. The portion distilling below 85° at 15 mm pressure is principally unaltered pinene. The remainder is saponified, and the resulting product is distilled. The yield of terpineol is 30 per cent of the theoretical. Bertram and Walbaum give the following method. Two kilograms of glacial acetic acid are mixed with 50 grams of water and 50 grams of sulphuric acid. Into the mixture, which should not be allowed to rise above 50°, 1 kg of rectified turpentine oil is poured, in portions of 200 grams at a time. After cooling and standing, the liquid is diluted with water and shaken with caustic soda solution. The product now consists of terpinene and terpinyl esters, which are

## P E R F U M E R Y

separated by fractional distillation. The esters, on saponification, yield terpincol.

**TERPINYL ACETATE.**—This ester of terpineol, of the formula  $C_{10}H_{17}OOC\ CH_3$ , is, from the legitimate point of view, of but little interest to the perfumer, as its odour, although refreshing, is too weak for it to be of much practical value. From the illegitimate point of view, it is, however, of considerable interest, as it is one of the artificial esters frequently used as an adulterant of essential oils containing esters. It is more especially used in the adulteration of lavender, petitgrain, and bergamot oils. It exists naturally in a number of essential oils, but is as a commercial product entirely manufactured artificially. If terpincol be heated under a reflux condenser with acetic anhydride and sodium acetate, it is converted into terpinyl acetate, but the conversion is not complete, the resulting product rarely containing more than 90 per cent of true ester. The best commercial samples have the following characters —

|                            |                    |
|----------------------------|--------------------|
| Specific gravity . . . . . | 0.958–0.965        |
| Optical rotation . . . . . | Almost inactive    |
| Refractive index . . . . . | 1.4648–1.4665      |
| Ester content . . . . .    | About 90 per cent. |

It is soluble in 5 volumes of 70 per cent alcohol. Terpinyl acetate is an ester which requires a much longer time for complete saponification than most other esters. Its presence can therefore be reasonably inferred if an essential oil gives a saponification value which is substantially higher after two hours' saponification than after thirty minutes', as most natural esters are saponified completely in the latter period.

**TERPINYL BUTYRATE.**—This ester has the formula  $C_{10}H_{17}OOC\ (CH_2\ CH_2\ CH_3)$ . It is an oil of characteristic fruity odour, and is useful in floral perfume mixtures. It has been found naturally, occurring in the oil from the New South Wales "mountain pine."

**TERPINYL CINNAMATE.**—The cinnamic acid ester of terpincol,  $C_{10}H_{17}OOC\ CH=CH\ C_6H_5$ , is a sweet fragrant oil, useful in the preparation of lilac, new-mown hay, and similar perfumes.

**TERPINYL FORMATE.**—This ester, of the formula  $C_{10}H_{17}OOCH$ , has been isolated from Ceylon oil of cardamom. It is a liquid of sweet odour, somewhat resembling the corresponding ester of citronellol or geraniol. It is used in the preparation

## P E R F U M E R Y

of some artificial neroli oils. It can be prepared either by the esterification of terpineol by formic acid or by the prolonged action of formic acid on turpentine. It has a specific gravity 0.998, optical rotation about  $\pm 69^\circ$ , and boils at  $135^\circ$  to  $138^\circ$  at 40 mm.

**TERPINYL PROPIONATE.**—This ester,  $C_{10}H_{17}OOC.CH_2.CH_3$ , has a distinct lavender odour. It is prepared by the esterification of terpineol by propionic acid. It is recommended for admixture with lavender and bergamot oils for cheap soap perfumery.

**TETRADECYL ALDEHYDES.**—The commercial article sold as " $C_{14}$ " aldehyde, or frequently as "peach aldehyde," is one of the most powerful of the higher aliphatic aldehydes, and although it is of great value in the rounding off of floral and fruity odours, it must be used in very minute quantities, or the composition will be ruined. It is in all probability a mixture of two or more isomers with, possibly, a lactone. The normal aldehyde has the formula  $CH_3(CH_2)_{12}CHO$ . A dimethyl-duodecyl aldehyde isomeric with the normal aldehyde exists, and has the formula  $CH_3(CH_2)_8.CH(CH_3)CH(CH_3)CHO$ . It is prepared in the following manner. Nonyl-methyl ketone is condensed with bromopropionic ester, zinc (activated with copper), and benzene (Reformatski's reaction). The hydroxy ester formed by the action of water on the organometallic condensation product is then dehydrated by means of phosphorus pentoxide which gives rise to methyl-nonyl acrylic ester, which on reduction yields dimethyl-duodecyl alcohol, and this is dehydrogenated to the aldehyde. (See *P. & E. O. R.*, 1924, 79.)

The normal aldehyde, with its intense peach odour, can be prepared from methyl myristate in the same manner as undecyl aldehyde (*q.v.*) from methyl laurate.

**TETRAHYDRO - para - METHYL - QUINOLINE.**—This body is a reduction product of methyl-quinoline, and is an evil-smelling liquid, resembling civet in odour. It is sometimes used as a substitute for civet, and enters into the composition of artificial civet.

**TETRANTHERA CITRATA.**—See "Litsea Oils."

**THUJA LEAF OIL.**—The leaves (and young twigs) of the leaves of *Thuja occidentalis* (*Arbor vitæ*) yield from 0.5 to 1 per cent. of essential oil. This has an odour similar to that of tansy, and is used in small quantities as a fixative. The principal odorous

## P E R F U M E R Y

constituent of the oil is the ketone thujone The pure oil has the following characters :—

|                               |              |
|-------------------------------|--------------|
| Specific gravity              | 0.910-0.935  |
| Optical rotation              | — 5° to — 16 |
| Acid value                    | 0.1          |
| Ester value                   | 18-27        |
| Ester value after acetylation | 36-45        |

The leaves and twigs of *Thuja plicata*, the Washington cedar, yield an essential oil of similar odour, also rich in thujone It has the following characters —

|                               |        |
|-------------------------------|--------|
| Specific gravity              | 0.913  |
| Optical rotation              | — 4.77 |
| Refractive index              | 1.4552 |
| Acid value                    | 0.5    |
| Ester value                   | 2.3    |
| Ester value after acetylation | 2.2    |

**THUJONE.**—Thujone,  $C_{10}H_{16}O$ , is the characteristic ketone found in the essential oils of thuja, tansy, wormwood, and sage, and is identical with the bodies originally described under the names tanacetone and salvone It is an oil of sharp aromatic and somewhat "heavy" odour. Wallach considers that there are two physically isomeric thujones, of which that in thuja oil is termed  $\alpha$ -thujone, and that in oil of tansy  $\beta$  thujone. Wormwood oil contains both isomers, the  $\beta$ - variety preponderating Sage oil also contains both isomers

The characters of  $\alpha$ -thujone are as follows .—

|                  |           |
|------------------|-----------|
| Boiling point    | 200°-201° |
| Specific gravity | 0.9125    |
| Refractive index | 1.4510    |
| Optical rotation | — 10°-23' |

$\beta$ -Thujone is a physical isomeride, but not the optical antipode of  $\alpha$  thujone. It has a specific rotation + 76.16'. (See E. J. Parry, "The Chemistry of Essential Oils," 4th ed, vol ii., pp. 235-237.)

**THUJYL ALCOHOL.**—This alcohol, having the formula  $C_{10}H_{17}OH$ , is found naturally in the essential oils of wormwood, thuja leaves and others, and also results from the reduction of the ketone thujone It is identical with the alcohol originally described as tanacetyl alcohol. There appears to be more than

## PERFUMERY

one body described under this name, Semmler having described the natural alcohol as having the following characters:—

|                                   |           |
|-----------------------------------|-----------|
| Boiling point . . . . .           | 210°–212° |
| Specific gravity at 20° . . . . . | 0.926     |
| Refractive index . . . . .        | 1.4635    |

Paolini (*Att. R. Accad. dei Lincei*, v., 20, i., 765) has separated from the reduction products of thujone an alcohol which he terms  $\beta$ -thujyl alcohol. This body has, when purified, the following characters:—

|                                   |                                    |
|-----------------------------------|------------------------------------|
| Boiling point . . . . .           | 206°                               |
| Specific gravity . . . . .        | 0.9187 at $20^{\circ}_{4^{\circ}}$ |
| Refractive index at 16° . . . . . | 1.4625                             |
| Specific rotation . . . . .       | + 116.9°                           |

**THYMBRA SPICATA, OIL OF.**—*Thymbra spicata* is a shrub belonging to the natural order *Labiatae*, and is indigenous to Greece and Asia Minor. Schimmel & Co. (*Report*, October, 1910, 147) have distilled the herb grown in Smyrna, and obtained 1.5 per cent. of a yellow oil having an odour of thyme and origanum. It had a specific gravity 0.946, refractive index 1.5067, and was optically inactive. It contained about 66 per cent. of carvacrol.

**THYME, OIL OF.**—The most valued oil of thyme is the French distillate, which is obtained from the fresh flowering herb in the mountains in the south of France. The plant used for distillation purposes is *Thymus vulgaris*. The oil has the following characters:—

|                            |                  |
|----------------------------|------------------|
| Specific gravity . . . . . | 0.900–0.935      |
| Optical rotation . . . . . | — 0° 30' to — 4° |
| Refractive index . . . . . | 1.4800–1.4950    |
| Phenols . . . . .          | 20–40 per cent.  |

The phenols present are mainly thymol mixed with a small quantity of carvacrol. There are two commercial varieties of the oil recognised, the red and the white. The red oil owes its colour to traces of metals, principally iron, derived from the stills and condensers used. By suitable rectification in vessels where there is no contact with iron, the white oil is obtained. It was some years ago a common practice to adulterate pale red oils with enormous quantities of oil of turpentine in order to produce a



## P E R F U M E R Y

"white thyme oil." These oils often contained only 1 or 2 per cent. of phenols, and are not now often found on the market.

Spanish oil of thyme has for some years been a market article, and was up till recently distinguished by its high phenol content, which consisted mainly of carvacrol, the oil having the following characters :—

|                  |                 |
|------------------|-----------------|
| Specific gravity | 0.928–0.958     |
| Optical rotation | + 2° to – 4°    |
| Refractive index | 1.5025–1.5115   |
| Phenols          | 50–75 per cent. |

The variable character of these phenols, which, although usually found to consist almost entirely of carvacrol, were from time to time found to be rich in thymol, caused considerable speculation as to the actual species yielding the oils. Mr H Rubeck, in 1920, obtained specimens of the plants which yielded oils so rich in thymol that it can be profitably manufactured therefrom, and caused them to be examined botanically. E. M. Holmes (*P. & E. O. R.*, 1920, 339) showed that the plant mainly responsible for the oil containing phenols which were almost entirely thymol was *Thymus zygis* var. *gracilis*. The species has a variety, *Thymus zygis* var. *floribunda*, which yields an oil almost free from thymol. The oil containing carvacrol is probably distilled from more than one species of *Thymus*, including *Thymus vulgaris*. According to the *Chemist and Druggist*, 1920, ii., 59, there are at least two dozen species of *Thymus* which occur in Spain, and several of them are of interest. The common thymes of these islands, *T. vulgaris* and *T. Serpyllum*, grow also in Spain, indeed the former, known as "Tomillo comun," is a native of Spain, and is said to have been introduced into Britain about 1548 or earlier. Spanish verbena oil is obtained from *T. hyemalis*, a species closely allied to the "lemon thyme," *T. citriodorus*. *T. Mastichina*, known as "Tomillo blanco," is also a well known species, which yields oil of wood marjoram, although in Portugal the wood marjoram or "ouregao do mato" is another species—i.e., *T. zygis*. *T. Mastichina* was used in Britain at the end of the eighteenth century as an errhine, under the name of *Marum vulgare* or common herb mastich. The flowers are white, not the usual purple; hence the Spanish name. Still another species is *T. Loscosii*, known as "Tomillo Sanjuanero." This is not at present of economic importance, but it is common in Aragon and elsewhere.

Interest at present, however, centres in the thymol-yielding species, *Thymus zygis* L., which adds one more to the list of

species containing this valuable phenol. These already included *T. vulgaris*, *Ocimum viride* of the Seychelles, *Monarda punctata* or American horsemint, among the *Labiatae*, and *Carum copticum* in the *Umbelliferae*. The distribution of these species, both geographically and botanically, suggests that there are still a number of undiscovered sources of thymol. The most important point in the botanical identification of the specimens sent to Mr. H. Rubeck is that they all belong to one particular variety of *Thymus zygis* L. There are two well-known varieties, namely, var. *gracilis* Boiss. and var. *floribunda* Boiss., and all the specimens yet examined are of the first kind. *Thymus zygis* L. var. *gracilis* Boiss. is therefore the correct botanical name of the new source of thymol. It is important that this should be recognised at an early stage, since it is quite probable that the var. *floribunda* may yield an oil with characters and content quite different from those of the oil obtained from var. *gracilis*. Producers of thymol should be quite certain of their raw material, and before var. *floribunda* is used a thorough investigation of a sample of the oil is suggested. In order to make identification of genuine var. *gracilis* easy, the differences between the two varieties are given below.

*Thymus zygis* L. is common almost throughout Spain and Portugal, occurring in oak and other woods, in deserts and dry gravelly places among the sierras of the central, eastern, and southern provinces; at Lérida and Balaguer, in Cataluna; at Fraga, Odon, Zaragoza, Benasque, Tarazona, and at an altitude of 5,000 feet on the Peña de Orocl, in Aragon; at Béjar, in León; at the monastery of Santa Espina, on Mount Torozo, at Valladolid, Venta de Baños, Alar de Rey, and Cervera, in Castilla la Vieja; at numerous places throughout Castilla la Nueva; at Muryiedro and Valldigna, in Valencia; at Archena and Albacete and on the Sierra de Segura, in Murcia; at numerous places throughout Andalucia; at Alange, Membrio, and in the environs of Plasencia, in Estremadura; and at Tras-os-Montes, in Portugal. As a consequence of its wide distribution, the common names for the plant vary greatly. In Portugal it is known as "Ouregao do mato," or wood marjoram; in the Balearic Islands it is called the "Señorida de flor blanca"; in Catalonia it is "Ferrigola" or "Farigola salsera"; but the Castilian names are still more varied. The most frequently occurring is "Tomillo salsero," or sauce thyme, from its use as a condiment; others are "Thymo de España," "Tomillo salsero de Toledo," "Tomillo aspero," or

rough thyme; "Serpul de peñas," or rock thyme; "Ajedrea menuda española," or common Spanish winter savory (the true winter savory is *Satureia hortensis*, another labiate); "Tomillo terrero," or humble thyme; "Tomillo aceitunero" and "Tomillo de aceitunas," or olive thyme; and "Almoradux de la tierra en Ronda," or sweet marjoram of Ronda.

The species *T. zygis* L. is very similar to *T. sylvestris* and *T. vulgaris*, but is easily distinguished by the comparatively large white hairs or cilia at the bases of the leaves. Linné noted this when he described the species as "*Facies T. vulgaris at Folia basi ciliata*." The flowers are described as purple or white, and the white form is evidently the only one occurring in the Balearic Islands. The two varieties were first described by Boissier ("Voy. bot. dans Le Midi de l'Espagne," 1839-45) under the name *T. tenuifolius*, but he afterwards agreed that his species, *tenuifolius*, was exactly the same as Linné's *T. zygis*. The species was known to Theophrastus as *Serpyllum zygis*, and var. *gracilis* is figured under that name by Barrelierus ("Icon. Plant. Gal. Hisp. et Ital.," Tab. 777, 1714).

*Thymus zygis* L. var. *gracilis* Boiss.—This variety differs from var. *floribunda* Boiss., in its simple branching habit. The linear leaves have their margins incurved to the midrib, and part of the lamina cannot be seen as in *floribunda*. The partial inflorescence is the usual cluster or verticillaster; in var. *gracilis* all the clusters are practically sessile in the axils of the bracts, but in *floribunda* the lower clusters are raised on quite long stalks. This is quite a striking difference when the plants are in bloom. The flower itself in var. *gracilis* has a short pedicel or stalk, while that of *floribunda* is quite sessile. The corolla is more deeply inserted into the calyx, and the long stamens are not exerted to the same extent as in *floribunda*. The calyx is two-lipped, with three ovate lobes in the upper and two ciliate awns in the lower lip. These lips diverge more in *gracilis* than in *floribunda*, the upper lip in the former being almost recurved in the mature calyx. At the throat of the calyx tube, on the inside, is a line of hairs, and this line dips down to the more deeply cleft lower lip in *gracilis*, whereas it is almost straight in *floribunda*. The stations recorded for var. *gracilis* are in Castilla la Nueva around Madrid in the Casa de Campo; in Murcia at Hellin, and between Totana and Lorca; in Andalucía between Alhama and the brow of Sierra Tejada, and in the pine woods of Puerta Real. This variety is therefore not such a decided alpine as var. *floribunda*, which occurs at an

## PERFUMERY

altitude of 3,500 to 4,000 feet in the environs of Chesa and Setiles, and at Molina, in Castilla la Nueva ; in Murcia ; and at an altitude of 3,000 to 5,000 feet on the Sierra de Gador, on the Sierra Nevada between Cadiar and Trevez, and on the heights of Granada in Andalucía.

It will be seen that, while some rather fine distinctions in the flowers are necessary to establish the identification of the varieties, they can be distinguished in the absence of the flowers by the greater recurving of the margins of the leaves in var. *gracilis*, and still more easily by the general habit ; var. *gracilis* when dried yields compact bundles of stems, each bundle being one plant, while var. *floribunda* yields a loose, somewhat tangled mass, because of the creeping rhizomatous habit of the main stem. The species as a whole is widespread and common, but it remains to be determined whether careful conservation, and possibly cultivation, are necessary ; var. *gracilis* is more easily collected on account of its lower stations, but those at present known are few, and further unguarded exploitation of the wild plant might result in the substitution of var. *floribunda*, with possible discredit to the reputation of Spanish thyme as a source of thymol.

Dr. Blaque obtained, by the distillation of 4.63 kg. of the flowering tips of *T. zygis* var. *gracilis*, 48.50 grams of essential oil, equal to 1.048 per cent. The oil has a light greenish-orange colour, and the characteristic odour of thyme oil. If left in a cool place, it deposits small crystals of thymol. On analysis it yielded 74.11 per cent. of total phenols, and 51.18 per cent. of crystallisable thymol. A sample of oil of *T. zygis* received direct from Barcelona was distilled for comparison, and gave 73.18 per cent. total phenols and 48.68 per cent. thymol. In all the analyses the thymol crystallised very rapidly in very pretty crystals.

According to Mastbaum (*Chem. Zeit.*, 1921, ii, 18), the oils richest in phenols distilled in Spain are those from *Corydolithymus capitatus*, whose phenol content is from 55 to 67 per cent.

The plant *Thymus mastichina*, the so-called wild marjoram of Spain, yields an oil which has been examined by Dorronsoro (in a paper read before the Soc. Españ. Fisic. y Quím., October, 1910). The oils upon which he worked included pure distillates of the years 1898, 1902, 1908, and 1909. The oil is a pale yellow to yellowish-green liquid, which darkens by keeping. The specific gravity varied between 0.907 and 0.945 at 20°, and the refractive index at 28° between 1.4630 and 1.4654. The optical rotation varied from - 0.7° to + 4.5°, and the oil was soluble in from

## P E R F U M E R Y

5 to 30 volumes of 40 per cent. alcohol. At 710 mm. the following fractions were obtained (from a 1909 distillate) :—

|         |              |   |   |               |
|---------|--------------|---|---|---------------|
| Between | 85° and 110° | . | . | 3.1 per cent. |
| "       | 110° " 160°  | . | . | 3.65 "        |
| "       | 160° " 170°  | . | . | 23.1 "        |
| "       | 179° " 180°  | . | . | 36.9 "        |
| "       | 180° " 195°  | . | . | 17.4 "        |
| Residue | .            | . | . | 25.9 "        |

The following table shows the characters of the fractions obtained by a distillation under reduced pressure (98 to 100 mm.) :—

| Temperature. | Per cent. | Refractive index<br>at 22°. | Rotation. |
|--------------|-----------|-----------------------------|-----------|
| To 100°      | 2.65      | 1.4600                      | + 3° 41'  |
| 100°-110°    | 43.0      | 1.4602                      | + 4°      |
| 110°-120°    | 28.55     | 1.4605                      | + 1° 58'  |
| 120°-125°    | 6.25      | 1.4617                      | 0°        |
| 125°-145°    | 10.25     | 1.4657                      | - 3°      |
| 145°-160°    | 3.75      | 1.4718                      | - 4° 10'  |
| 160°-175°    | 3.05      | 1.4784                      | - 1° 55'  |
| Residue      | 2.5       | —                           | —         |

The five samples of oil examined had the following characters :—

|                               | 1898.           | 1902.           | 1908.           | 1909.          | 1909.          |
|-------------------------------|-----------------|-----------------|-----------------|----------------|----------------|
| Saponification value          | 18.5            | 14.3            | 16.3            | 12.7           | 17.4           |
| Esters as linalyl acetate     | 6.47 per cent.  | 5 per cent.     | 5.7 per cent.   | 4.41 per cent. | 6.09 per cent. |
| Ester value after acetylation | 42.4            | 38              | 49.3            | 29.2           | 45.6           |
| Free alcohols as linalol      | 12.05 per cent. | 10.75 per cent. | 14.09 per cent. | 8.20 per cent. | 13 per cent.   |

The author considers that the oil has the following approximate composition : *d* pinene, 7 to 8 per cent. ; eucalyptol, 64 to 72 per cent. ; phenols, less than 0.1 per cent. ; ketones, less than 0.1 per cent. ; esters, 4 to 6.5 per cent. ; and free alcohols, 8 to 14 per cent.

Leone and Angelescu (*Gazzetta*, 1922, 52, i., 152) have examined the oil obtained by the steam distillation of the dried plant *Thymus straius*, of Italian origin. They obtained 0.342 per cent.

of a lemon-yellow oil with a powerful aromatic odour. It had a specific gravity at  $\frac{0^{\circ}}{4^{\circ}}$ , 0.9181; refractive index, 1.4937 at  $24^{\circ}$ ; and optical rotation,  $-4.3^{\circ}$ . The oil contained 30 per cent. of thymol, about 9.5 per cent. of alcohols, 3 per cent. of esters, and hydrocarbons consisting principally of cymene. A small amount of a sesquiterpene was also present.

J. C. Umney (*P. & E. O. R.*, 1914, 423) examined three samples of oil from *Thymus vulgaris* which were of exceptional interest. The oils were distilled in British East Africa from plants grown from seeds obtained from Messrs. Sutton & Co., of Reading, and from young plants obtained from the same source, and from seeds obtained from a French source.

The oils had the following characters:—

| Source.            | Yield.<br>Per cent. | Specific<br>gravity. | Phenols.<br>Per cent. | Refractive<br>index. |
|--------------------|---------------------|----------------------|-----------------------|----------------------|
| English seeds . .  | 0.5                 | 0.901                | 32                    | 1.4900               |
| English plants . . | 0.7                 | 0.905                | 32                    | 1.4768               |
| French seeds . .   | 0.38                | 0.905                | 40                    | 1.4908               |

*Thymus capitatus* yields an oil having a specific gravity about 0.900, containing both thymol and carvacrol. *Thymus camphoratus* yields a similar oil.

Pellini (*Ann. di Chim. Applic.*, vii., fasc. iii.) states that the oil from *Thymus capitatus* grown in Sicily differs entirely from the Spanish oil from the same plant. The oil examined by him had the following characters:—

|                            |                 |
|----------------------------|-----------------|
| Specific gravity . . . . . | 0.950           |
| Optical rotation . . . . . | $-0^{\circ}53'$ |
| Refractive index . . . . . | 1.5048          |
| Acid value . . . . .       | 3.5             |
| Ester value . . . . .      | 3.5             |
| Phenols . . . . .          | 67 per cent.    |

The phenols were found to consist almost entirely of carvacrol.

Essential oil of *T. capitatus* is being produced in Spain on an increasing scale, and it deserves investigation on the ground of its high phenolic content. It is sold largely as oil of thyme, and the species yielding it is very plentiful in Tunisia.

For a long time *T. capitatus* has been used in medicine. It was formerly known as Cretan thyme, and its flower heads figured in

the French Codex of 1818. It is very common in all the warm regions of the Mediterranean zone. In Spain the plant is very abundant in the south and south-east, and especially in Granada, Cadiz, Seville, Huelva, Malaga, and Cordova. America is the chief customer for the oil. In southern Italy it grows profusely, and its cultivation and distillation in Sicily have recently been suggested.

Until the last few years the chemical composition of oil of *T. capitatus* seems to have been very imperfectly known. Gildemeister (Gildemeister and Hoffmann, iii, p. 533) reported the results of an analysis by *Schimmel & Co.*, which ascribed to this oil the following characters: A strong odour of thyme recalling a little that of *origanum*; specific gravity, 0.901; slight content of thymol, only about 6 per cent.; also contains a liquid phenol, apparently carvacrol.

In 1922, Palazzo, in a study of the oils of *T. capitatus* distilled in Sicily, indicated that they contained about 75 per cent. of phenols almost entirely composed of carvacrol, at the same time this author mentioned the wide difference between his results and those reported by Gildemeister. Dr. Blaque has fully confirmed Palazzo's statement, and has only verified one point in *Schimmel's* analysis, that is, that oil of *T. capitatus* has an odour reminiscent of *origanum*. The oils studied by Dr. Blaque came from two different countries. (1) Spain, about Malaga, and (2) Tunisia. Spanish *T. capitatus*: A lot of 3.770 kg. of the entire flowering plant gave, when distilled, 39 grams of oil, or 1.034 per cent. The oil contained 63.98 per cent. of total phenols. No trace of thymol could be crystallised, hence the proportion of carvacrol must be very high. Tunisian *T. capitatus*: 4.800 kg. of the entire flowering plant distilled yielded 90 grams of oil, or 1.875 per cent. Total phenols in the oil equalled 52.91 per cent. The presence of thymol could not be detected. Both oils have a strong orange colour and the same odour of thyme and marjoram, the phenols in both cases being almost entirely composed of carvacrol.

*Thymus hyemalis* yields the so-called Spanish verbena oil. (See "Verbena Oil.")

For the determination of thymol the usual method of absorption by 5 per cent. solution of caustic soda is usually adopted. Kremers recommends the following method:—

Five cubic centimetres of the oil are weighed and transferred to a glass-stoppered burette graduated in  $\frac{1}{10}$  c.c., and diluted with about an equal volume of petroleum ether. The mixture is well

## P E R F U M E R Y

shaken with a 5 per cent. solution of potassium hydroxide and allowed to stand until separation takes place. The alkaline solution is then run off and transferred to a 100 c.c. graduated flask. This operation is repeated until no further decrease in the volume of the oil takes place. The alkaline solution of thymol is made up to 100 c.c. or 200 c.c., as may be required, with a 5 per cent. caustic soda solution. To 10 c.c. of this solution in a graduated 500 c.c. flask is added a decinormal iodine solution in slight excess, whereupon the thymol is precipitated as a brown iodine compound. In order to ascertain whether enough iodine has been added, a few drops are transferred to a test tube, and a few drops of dilute hydrochloric acid are added. If sufficient iodine has been added, the solution remains brown; otherwise the liquid is milky white, on account of the separation of thymol. If an excess of iodine is present, the solution is slightly acidified with dilute hydrochloric acid, and diluted to 500 c.c. From this, 100 c.c. are filtered off, and the excess of iodine determined by titration with decinormal solution of sodium thiosulphate. Each cubic centimetre of decinormal iodine solution consumed is equivalent to 0.003753 gram of thymol.

**THYMENE.**—This name is applied to the waste product obtained from oils rich in thymol. The residue always contains a small quantity of thymol and has an odour allied to thyme, and is sold for cheap soap perfumery. It consists mainly of hydrocarbons.

**THYMOL.**—Thymol is a phenol, having the constitution of isopropyl-*meta*-cresol,  $C_{10}H_{14}O$ . It is the principal constituent of many varieties of thyme oil, and of ajowan seed oil, and is also produced by artificial methods. It is a colourless crystalline compound having a characteristic odour of thyme oil, melting at  $50^{\circ}$  to  $52^{\circ}$ , and boiling at  $232^{\circ}$  to  $234^{\circ}$ . It occurs in numerous essential oils, the proportions in the principal oils being as follows (Pelini, *Ann. di Chim. Applic.*, vii., fasc. iii.) :—

|  | Per cent. |
|--|-----------|
| <i>Monarda punctata</i> (United States)    | 64-80     |
| <i>Thymus vulgaris</i> (Spain)             | 50-70     |
| <i>Origanum hirtum</i> Lk. (Spain)         | 50-60     |
| <i>Ptychotis Ajowan</i> D. C.              | 45-55     |
| <i>Origanum virens</i> var. <i>siculum</i> | 50        |
| <i>Mosla japonica</i> Maxim.               | 44-50     |
| <i>Canila mariana</i> L.                   | 40        |
| <i>Thymus vulgaris</i> (Italy)             | 38        |
| „ „ {Africa or England)                    | 32-40     |



## P E R F U M E R Y

|   | Per cent. |
|---|-----------|
| <i>Ocimum viride</i> (Sierra Leone) . . . . . | 32        |
| <i>Thymus vulgaris</i> (France) . . . . .     | 20-40     |
| <i>Thymus striatus</i> (Italy) . . . . .      | 30        |
| <i>Monarda punctata</i> . . . . .             | 20-30     |
| <i>Origanum floribundum</i> M. . . . .        | 25        |
| <i>Thymus vulgaris</i> (Germany) . . . . .    | 20-25     |
| <i>Satureja thymbra</i> . . . . .             | 19        |
| <i>Thymus capitatus</i> (Spain) . . . . .     | 6         |
| <i>Origanum vulgare</i> (Rome) . . . . .      | 2.2-6.7   |

Thymol combines with chloral to form a compound melting at 131° to 134°. The phenyl-urethane melts at 107°.

Thymol is prepared from those oils which are sufficiently rich in it, by extracting the oil with a caustic soda solution, and liberating the thymol from the alkaline solution thus obtained.

For details concerning the determination of thymol, see "Thyme Oil" and "Phenols, Determination of." Thymol, like carvacrol, can be removed from alkaline solution either by steam distillation or by extraction with ether.

Blaque, in a brochure published on essential oils containing thymol (Paris, 1923; *P. & E. O. R.*, 1923, 154), advocates the use of the oil from *Ocimum gratissimum* for the extraction of thymol. He gives the following account of the plant (see also "Basil, Oil of") :—

*O. gratissimum* is a vigorous plant from 1 to 1½ metres high. It is widely spread in the East Indies, Ceylon, and Java; in tropical Africa and tropical America. According to M. Rolland, the cultivation in the Ivory Coast presents no difficulties. The seeds are sown in a nursery, and the young plants transplanted when about 25 cm. high. The seedlings soon put forth a vigorous stem, and can, in favourable situations, reach 1.80 metres high. The harvest is made at the moment of flowering by cutting the flower heads with a sickle. The plants grow so vigorously that a second cutting is possible in the same year, or even a third if the rains have been copious. Exceptional dryness is injurious. The distillation of the flower heads should be done immediately after cutting; if allowed to dry, the yield of oil is poor. An average yield is 0.60 per cent. by weight of the fresh herb. After a time, especially if stored in a cool place, small crystals of thymol are deposited. An analysis of the oil from Dabakala showed 56.29 per cent. total phenols, and 39.15 per cent. crystallisable thymol. These results are slightly below the *Roure-Bertrand* figures. This is explained by the analytical processes employed, that used by

## P E R F U M E R Y

the Grasse firm being Gildemeister's method, which may give too high results. In 1917 the Imperial Institute examined an oil from the Seychelles from cultivated plants introduced some years previously. Their results showed 62 per cent. phenols, mainly eugenol. This result differs widely from those given by the Ivory Coast oil, and although Kew has stated that the Seychelles plant is *O. gratissimum*, the author believes that it is a different plant from that cultivated for more than ten years at Dabakala. However that may be, the results of Dr. Blaque's examination confirm him in the opinion that *O. gratissimum* is an excellent source from which to obtain thymol, particularly as at least two crops may be expected annually. Possibly, he adds, also ajowan could be introduced into French northern Africa, where allied species already exist, and, bearing in mind the acclimatisation of ajowan in the Seychelles, it could perhaps be cultivated successfully in Madagascar, the Comoro Isles, and Réunion. The author further suggests that *T. zygis* should be introduced in the wastes of the province of Languedoc, so that France might possess a plant richer in thymol than *Thymus vulgaris*. Whilst *O. gratissimum* has already been cultivated with good results in the Ivory Coast, it would be advisable to study, as regards oil yield and thymol content, the effect of different soils, exposures, etc., and to endeavour to establish special strains of industrial value.

Dr. Blaque also gives a summary of the principal thymol-producing plants of the world (see table on p. 757).

There are numerous methods for the artificial preparation of thymol, many of which are the subjects of patents. In the present state of our knowledge of these processes, the almost universal drawback to them is that the yield of thymol is too small to allow the process to be commercially payable. Amongst the most interesting of these processes is that originated by Smith and Penfold (*Jour. and Proc. Roy. Soc. N.S.W.*, liv., 40), depending on the oxidation of piperitone, the so-called "peppermint ketone" of certain species of *Eucalyptus*, especially *Eucalyptus dives*. In this method 60 grams of pure piperitone are added to a solution of 175 grams of ferric chloride, 160 c.c. of glacial acetic acid, and 500 c.c. of water. The whole is then heated to boiling point on a sand bath for an hour, when the reaction takes place as follows:—



the piperitone being thus oxidised to thymol, with a molecular rearrangement. The reaction product is steam distilled, the

# PERFUMERY

Percentages of Oil and Thymol in Plants

| Plant.                                 | Place of origin of sample. | Part of plant distilled. | Percentage of oil. | Percentage in oil of |                        |
|--|----------------------------|--------------------------|--------------------|----------------------|------------------------|
|  |                            |                          |                    | Total phenols.       | Crystallisable thymol. |
| <i>Carum copiticum</i>                 | B India.                   | Seeds                    | 3.4                | —                    | 45.50                  |
| "                                      | Seychelles                 | "                        | "                  | —                    | 38                     |
| "                                      | Montserrat.                | "                        | 3.1                | —                    | 54                     |
| "                                      | Militz                     | Entire plant.            | 0.12               | —                    | 1                      |
| <i>Thymus zygis</i>                    | Spain                      | Flowering plant.         | 1.018              | 74.11                | 51.18                  |
| <i>Ocimum gratissimum</i>              | Ivory Coast.               | Stems and leaves.        | 0.60               | 56.29                | 39.15                  |
| " <i>viride</i>                        | Seychelles                 | Leaves                   | 0.50               | 62                   | ?                      |
| "                                      | "                          | Flower heads             | 0.15               | 52                   | ?                      |
| "                                      | "                          | Leaves                   | 0.35               | —                    | 32                     |
| "                                      | Sierra Leone.              | "                        | —                  | —                    | 37                     |
| "                                      | Seychelles.                | Flower heads.            | 1.3                | —                    | 50                     |
| "                                      | Japan.                     | "                        | 0.30-0.40          | 72.74                | 64.3                   |
| <i>Mosla japonica</i>                  | United States.             | Leaves.                  | 0.27               | 60.4                 | 44                     |
| <i>Monarda punctata</i>                | Montserrat                 | Flowering plant.         | 1.034              | 63.98                | ?                      |
| "                                      | Spain.                     | "                        | 1.875              | 52.91                | ?                      |
| <i>Thymus capitatus</i>                | Tunisia                    | "                        | 0.884              | 57.23                | ?                      |
| "                                      | Morocco                    | "                        | 0.4-0.5            | —                    | 20-30                  |
| "                                      | France                     | Entire plant.            | 0.7                | 40                   | ?                      |
| "                                      | United States              | "                        | —                  | —                    | 19                     |
| <i>Camula mayana</i>                   | Spain.                     | Flowering plant          | 1.106              | —                    | 50                     |
| <i>Satureja thymbra</i>                | Sicily.                    | Entire plant.            | 3.3                | 66-67                | 51-60                  |
| <i>Origanum vulgare</i>                | Dalmatia.                  | "                        | —                  | 57-74                | ?                      |
| " <i>hirtum</i> var. <i>albiflorum</i> | Syria.                     | "                        | —                  | —                    | 25                     |
| " <i>maru</i>                          | Algeria.                   | "                        | —                  | —                    | —                      |
| " <i>floribundum</i>                   | "                          | "                        | —                  | —                    | —                      |

## P E R F U M E R Y

phenol extracted from the distillate by a 5 per cent. caustic soda solution, the solution decomposed by hydrochloric acid, and the liberated thymol purified by distillation under reduced pressure.

The condensation of *meta*-cresol with isopropyl alcohol, with thymol as the result, was first described by Mazzara (*Gazz. Chim. Ital.*, 12, 505). J. W. Blagden has recently taken out a British patent (No. 197848) based upon this method, in conjunction with Howards & Sons, Ltd. This patent contains the following details :—

Thymol has been made by condensing mono-sulphonated *meta*-cresol with isopropyl alcohol, but the condensation is accompanied by the formation of a number of by-products, so that the yield of thymol is not large, and its purification is difficult. By the present invention these by-products are in large measure or completely avoided by condensing polysulphonated *meta*-cresol with isopropyl alcohol. For this purpose, the cresol may first be sulphonated under conditions adapted to produce di- or even tri-sulphonic acid of cresol, and the product may be condensed with isopropyl alcohol; the sulphonic acid groups are afterwards eliminated by suitable treatment, such as by the action of steam. For example, 54 parts by weight of *meta*-cresol may be added slowly, while cooling, to 125 parts of oleum containing about 88 per cent. of total  $\text{SO}_3$ , and the mixture heated for several hours, for instance, two hours at  $100^\circ \text{C}$ ., and finally for two hours at  $150^\circ \text{C}$ . To the mixture may be added slowly a solution of 35 parts of isopropyl alcohol in 50 parts of sulphuric acid of 98 per cent strength, and the mixture stirred for several hours at  $80^\circ$  to  $90^\circ \text{C}$ . The mixture may then be kept at a temperature of about  $130^\circ \text{C}$ . and treated with a current of steam, whereby the thymol is distilled. After removing a small quantity of a by-product in alkali, 50 to 55 parts of oil are obtained which consists chiefly of thymol and contains little of the isomer melting at  $114^\circ \text{C}$ .

Phillips and Gibbs (*Jour. Ind. Eng. Chem.*, 1920, 733) have summarised the history of the artificial preparation of thymol, and for many interesting details reference may be made to their paper. Phillips (*Jour. Amer. Chem. Soc.*, 1923, 45, 1489) gives the following account of his improved process for the manufacture of thymol from *para*-cymene, the original process having been described in the *Journal of Industrial and Engineering Chemistry* (*loc. cit.*) :—

(1) *Cymene from sulphæe liquor*.—The liquor is distilled in

steam, and the oil washed first with NaOH to remove  $\text{SO}_2$ , and then with water. It is dried over  $\text{CaCl}_2$  and distilled over sodium, the fraction  $176^\circ$  to  $178^\circ$  being collected.

(2) *Nitration*.—Two thousand one hundred and forty-four grams of cymene are stirred with 2,460 grams of concentrated  $\text{H}_2\text{SO}_4$  at  $0^\circ$ , and mixed acid (3,280 grams  $\text{H}_2\text{SO}_4$  and 1,624 grams  $\text{HNO}_3$  of density 1.42), previously cooled to  $0^\circ$ , is slowly added during sixteen hours, the temperature being kept at  $0.5^\circ$ . After stirring for another hour, the liquid is allowed to settle, and the lower layer removed. The upper layer is washed free from acid (with water only, to avoid emulsification) and the nitrocymene is distilled off in superheated steam as a yellow oil, heavier than water. Yield, 45 to 50 per cent. of theoretical.

(3) *Reduction to Cymidine*.—To a boiling mixture of 1,600 grams of iron powder, 1.5 litres of water, and 100 c.c. of concentrated HCl are added 1,000 grams of nitrocymene at such a rate as to keep the mixture boiling quietly. When there is no further heat evolved on shaking, reduction is complete. The whole is made alkaline with NaOH, and the cymidine is distilled off in steam as a light oil. Yield, 80 to 85 per cent. of theoretical.

(4) *Sulphonation*.—Three parts of cymidine are suspended in 2 parts of concentrated  $\text{H}_2\text{SO}_4$ , and 6 parts of 20 per cent. oleum are added at such a rate that the temperature does not exceed  $140^\circ$ . The whole is then heated at  $130$  to  $140^\circ$  (inside temperature) until a sample is completely soluble in caustic soda (about 30 to 45 minutes). The melt is poured into 3 volumes of ice water and, after standing two hours the precipitated cymidine-sulphonic acid is filtered off. The product is purified by solution in 20 per cent. NaOH, decolorising with animal charcoal, and reprecipitating with excess of  $\text{H}_2\text{SO}_4$ . The white crystalline powder is dried at  $120^\circ$ . Yield, 80 per cent. of theoretical.

(5) *Diazotisation and Reduction*.—Two hundred and twenty-nine grams of cymidine-sulphonic acid are suspended in a litre of water, and slight excess of NaOH is added. The mixture is warmed until all is dissolved, then cooled to  $0^\circ$  and mixed with 69 grams of sodium nitrite (as 20 per cent. solution). The whole is now added slowly to 150 grams of  $\text{H}_2\text{SO}_4$  in a litre of water at  $0^\circ$ , and well stirred. The precipitated diazo compound is filtered off and added to a solution of 300 grams of  $\text{Na}_2\text{SO}_3$  in 3 litres of water which has been saturated with  $\text{SO}_2$ . After standing at room temperature for an hour, the mixture is heated to the boil, 500 c.c. of concentrated HCl are added, and the solution is evaporated to

crystallisation. Yield of cymylhydrazine-sulphonic acid, dried at  $110^{\circ}$ , is 70 to 75 per cent. of theoretical.

(6) *Sodium Cymene-sulphonate*.—A solution of 244 grams of cymylhydrazine-sulphonic acid in hot water is added in portions to a boiling 10 per cent. solution of  $\text{CuSO}_4$ . Excess of copper sulphate should be present (indicated by persistence of the blue colour). The filtered liquid is treated with slight excess of baryta water, filtered from  $\text{BaSO}_4$  and  $\text{Cu}(\text{OH})_2$ , and excess baryta removed by a current of  $\text{CO}_2$ . The final filtrate is evaporated to dryness, and the residual sodium sulphonate dried at  $140^{\circ}$ . Yield, 79 per cent. of theoretical.

(7) *Thymol*.—The best yield is obtained by melting 1 part of dry sulphonate with 2 to 3 parts of  $\text{KOH}$  at  $350^{\circ}$  for half an hour. The cooled melt is dissolved in water, acidified with  $\text{H}_2\text{SO}_4$  and extracted with ether. The extract is dried, ether evaporated, and the thymol fractionally distilled. Yield, 59 per cent. of theoretical. The product solidifies completely when seeded with a crystal of thymol. It gives a phenylmethane melting at  $107^{\circ}$ , and is free from carvacrol.

(See also U.S.P., patent No. 1378939 of May 24th, 1921, of R. M. Cole)

The so-called spruce turpentine, a hydrocarbon liquid separating in the sulphite process of manufacturing wood pulp from spruce wood, contains a large quantity of cymene. R. H. McKee has obtained a United States patent for the manufacture of thymol from this waste product (See *P. & E. O. A.*, 1923, 198.)

The "spruce turpentine" is ordinarily collected in separating funnels containing an acid solution of calcium bisulphite, through which the gases and vapours from the digesters pass, the oil collecting on the surface of the acid liquor, from which it is drawn off from time to time. The oil, as thus obtained, contains impurities, including sulphur dioxide and tarry bodies. It is purified by a single or by repeated distillation in the presence of steam, until about 80 or 90 per cent. of the oil is obtained as a distillate. A single distillation usually suffices for Mr. McKee's process.

The distillate then has its water removed by passing the liquid over or through calcium chloride, or by heating it until about 2 per cent. has been vaporised.

Carvacrol is produced by treating the purified "spruce turpentine" with sulphuric acid, converting the sulphonic acid formed into an alkali metal salt, fusing such salt with a caustic alkali, and adding an acid to the resulting mass. A small amount, usually

## PERFUMERY

about 5 per cent. of thymol is produced, and the proportion of thymol to carvacrol produced can be increased by using fuming sulphuric acid (20 per cent. oleum) to 15 or even 20 per cent. of the product. The carvacrol and thymol can then be separated.

In practice, the purified spruce turpentine is treated with approximately its own volume of fuming sulphuric acid (20 per cent. oleum) at 25° to 30° C., or not above 50° C., to avoid the formation of undesirable disulphonic acids. To the resulting mass, consisting of a mixture of the 1 : 2 : 4 and 1 : 3 : 4 sulphonic acids, together with excess sulphuric acid, is then added lime or calcium carbonate until the acids are substantially neutralised or rendered slightly alkaline; the resulting calcium sulphate is separated by filtration. The filtrate—calcium salts of the sulphonic acids—is then converted into the corresponding salts of sodium by adding sodium carbonate, the solution is filtered, and the sodium sulphonic acid salts separated by evaporation, fused with caustic soda, the fused mass dissolved in water and neutralised with sulphuric acid, yielding a mixture of approximately 80 to 85 per cent. of carvacrol and 15 to 20 per cent. of thymol, which may be separated from the mass by distillation.

McKee prefers to partially evaporate the solution of the calcium salts of the 1 : 2 : 4 and 1 : 3 : 4 sulphonic acids to permit the crystallisation out on cooling of a part of the calcium salt of the 1 : 2 : 4 sulphonic acid. The evaporation is so conducted as to permit about two-thirds of the dissolved salts to crystallise out. The crystals are separated by filtration and washed with a small amount of water. The filtrate and wash water contain the calcium salt of the 1 : 3 : 4 sulphonic acid together with some of the 1 : 2 : 4 sulphonic acid salt. In practice, this liquid ordinarily contains about equal parts by weight of the 1 : 2 : 4 and 1 : 3 : 4 acid salts. To this liquid is then added a soluble sodium salt, preferably a solution of soda ash, and after separating by filtration the precipitated calcium carbonate produced, the resulting solution of sodium sulphonic acid salts is evaporated to dryness, fused with a caustic alkali, preferably caustic soda, and the fused mass dissolved in water and neutralised with an acid, such as sulphuric acid, yielding approximately equal parts by weight of carvacrol and thymol, which may be separated from the mass by decantation or steam distillation.

To the carvacrol-thymol mixture produced as first described, or in accordance with the preferred procedure, is added approxi-

## PERFUMERY

mately 3 parts by weight of preferably finely-ground, well-dried lead acetate, and the mixture allowed to stand for several hours, preferably twenty-four, at room temperature, and the resulting mass broken up and washed with a volatile petroleum hydrocarbon, preferably gasoline. The thymol-lead acetate addition product obtained is insoluble in the gasoline, while carvacrol and the carvacrol-lead acetate addition product, which is formed with difficulty, are soluble in gasoline, and are removed in the washing operation described.

The thymol-lead acetate compound is then distilled with steam, the thymol passing over with the steam, and the lead acetate solution evaporated to dryness for re-use. The resulting thymol is preferably further purified by distillation.

The carvacrol-containing filtrate is separated from the gasoline by distillation, and the carvacrol separated from the remaining portion by distilling with steam, as described above, and the product further purified by distillation.

In the use of fuming sulphuric acid it is not necessary to employ the particular strength referred to. The proportion of the thymol derivative varies with the strength of the acid used, so that a desired strength of acid may be selected in accordance with the results aimed at.

According to the *P. & E. O. R.*, 1924, 317, a co specification (221226), dated August 30th, 1924, for a British patent for a process for the preparation of thymol from 2-cymidine has been filed, and is open to inspection under the International Convention. The applicant is Geza Austerweil, of Boulogne-sur-Mer. By the process 2-cymidine is copulated with an aromatic diazo compound to form an ammo-azo dye; this dye is deaminated, cut in two by reduction, and the cymidine obtained in this way (which is an isomer of the original cymidine) is transformed into thymol by diazotisation and boiling.

If 2-cymidine, obtained from the normal 2-nitro-cymene by ordinary reduction or otherwise, is copulated with a diazotised aromatic amino-sulphonic or amino-carbonic acid, or even with diazotised 2-cymidine itself, to form a diazo-amino dye, and this is then isomerised to the corresponding amino azo dye, the copulation takes place at the para-position to the original amino group of the 2-cymidine. If the free residuary amino group of this amino-azo dye is eliminated and the dye molecule cut in two with reducing substances, then the applied first component of the dye is obtained back again, and the second scission product is an amine,



a new cymidine, which contains the amino group in meta-position of the methyl group, and in the para-position of the eliminated amino group of the originally introduced 2-cymidine; this new amine is 5-cymidine, and if this is diazotised and boiled with acids or alkaline solutions the resulting phenol is thymol.

The same copulation can also be obtained if the 2-cymidine is treated in the presence of an aromatic amine and amino-chlorhydrate with the diazotised solution of the other component (for instance, an amino-sulphonic acid), the dye obtained separated, and its free amino group again diazotised, and so eliminated by known methods. One may also acetylise the 2-cymidine and copulate it directly with the diazotised first component of the dye, but without the addition of an amine, as the copulation takes place now directly in para-position to the substituted (acetylisied) group of the 2-cymidine; this dye is heated with dilute alkaline or acid solutions to saponify the acetyl group; then the free amino group is diazotised and treated as before. If the 2 molecules of cymidine were copulated, only one of them is transformed into 5-cymidine, and there is only a yield of one molecule of thymol; one molecule of 2-cymidine (the one which was diazotised) is obtained back again as such.

*Example I.*—One hundred grams of dry sulphanilic acid are dissolved in a 3 per cent. soda solution; to this solution a solution of 230 c.c. of 20 per cent. sodium nitrite is added; the whole is cooled, and the theoretical amount of 15 to 20 per cent. hydrochloric acid solution is added to it. Then 75 grams 2-cymidine are dissolved in dilute hydrochloric acid and slowly added to the diazotised solution; at the end of this operation concentrated sodium-hydrogen solution is carefully added till the mass is alkaline; the diazo-amino dye precipitates, is filtered off and dried. In its dry state it is mixed with its own weight of aniline and heated 2 hours to 50 to 60° C. This reaction mass is poured into dilute acetic acid, sufficient to neutralise the free amino present; the amino-azo dye now precipitates. It is filtered off, suspended in dilute hydrochloric acid, and the calculated amount of sodium nitrite is added; the so diazotised amino group is thus eliminated with the help of reducing agents. The residual product is diluted with hot water and reduced hot with the calculated amount of sodium hydrosulphite, titanous chloride or stannous chloride; the sulphanilic acid precipitates from the acid solution on cooling; it is filtered off, the solution is made alkaline, and the 5-cymidine taken up with benzene. From this solution it is precipitated in

the form of hydrochloride, diazotised and boiled, and thus yields thymol

*Example II*—One hundred grams of naphthylamine sulphonie acid, dissolved in a diluted soda solution, are diazotised, and, as described in Example I, copulated with 63 grams of acetyl-2-cymidine to form an amino-azo-dye. This dye is salted out, filtered off, deacetylisèd, and the free amino group eliminated; it is then treated as described in Example I.

Complete specification No. 221227, applicant G. Austerweil, and dated August 30th, 1924, is also open to inspection. It concerns the preparation of thymol from *p*-cymene. Such preparation is difficult because thymol is a 5-hydroxy-1-methyl-1,4-isopropylbenzene, and the attack of the cymene molecule, which is a 1-methyl-4-isopropylbenzene, occurs regularly in ortho position of the 1-methyl group, but the difficulty is obviated in accordance with this invention by the reduction of 2-nitro-cymene (which is readily obtained from *p*-cymene) to products which contain an oxygen atom attached to the nitrogen, isomerisation of these products with acids, to oxyderivatives in which the oxygen is in para-position to the nitrogen, and subsequent elimination of the nitrogen.

The 2-nitrocymene is reduced in such a way that there remain oxygen-containing groups or an oxygen atom attached to the nitrogen of the 2-nitrocymene; these intermediary reaction products are isomerised with concentrated sulphuric acid in para-substituted derivatives, so that the oxygen-containing radicals, and in consequence the oxygen itself, goes into the para-position of the former nitro group, *i.e.*, into the position where the oxygen of the thymol is situated. The nitrogen is eliminated afterwards in the form of an amino group.

Such isomerisable reduction products of the nitro-cymene are, for instance, the azo-oxy-cymene and the cymylhydroxylamine. The first can be obtained either by electrolytic reduction of the nitrocymene in alkaline solution or by an energetic reduction in an alcoholic alkaline solution; the hydroxylamine derivative is easily obtained through the reduction of the nitrocymene in a neutral salt-containing solution. The azo-oxy-cymene isomerised with concentrated sulphuric acid gives a mixture of *p*-oxy and *o*-oxy azo-cymene, these two bodies are identical from the point of view of the production of thymol because of the symmetry of the cymene molecule. Cymylhydroxylamine gives with concentrated sulphuric acid, and also dilute sulphuric

## P E R F U M E R Y

acid, *p*-amino thymol with a quantitative yield. The oxyazocymene molecules are cut in two with hydrosulphite, giving 2-aminocymene (2-cymidine) and *p*- and *o*-aminothymol with an excellent yield. These bodies are separated by distillation, and the amino group is eliminated from the aminothymols by known methods.

**THYMOL METHYL ETHER.**—This body is found in the essential oil of *Crithmum maritimum*. It is an oil of the formula  $C_{11}H_{16}O$ , having a specific gravity 0.954 at  $\frac{0^\circ}{4}$ , and boiling point,  $214^\circ$  to  $216^\circ$ . It has a sharp aromatic odour.

**THYMOHYDROQUINONE.**—This compound,  $C_{10}H_{14}O_2$ , is found in the essential oils of *Monarda fistulosa*, *Thuja articulata*, and *Callitris quadrivalvis*. It forms crystals melting at  $143^\circ$ , and boiling at  $290^\circ$ . Its dimethyl ether,  $C_{12}H_{18}O_2$ , is present in the oil of *Eupatorium triplinerve* and in arnica root oil.

**THYMOQUINONE.**—This body has the constitution  $C_6H_2(O_2)(CH_3)(C_3H_7)$ . It is present in the essential oils of *Monarda fistulosa* and *Thuja articulata*. It forms fine crystals melting at  $48^\circ$ , and boiling at  $98^\circ$  to  $100^\circ$  at 6 mm. It has a phenolic odour.

**TIGLIC ACID ESTERS.**—Schimmel & Co. (*Bericht*, Oct., 1913, 61) have succeeded in preparing synthetically geranyl, citronellyl, and phenyl-ethyl tiglates, esters which are present in Bourbon and other geranium oils, and which are mainly responsible for the characteristic odours of these oils. The esters were prepared by the action of tiglic acid chloride on the alcohols in question in the presence of pyridine. The three esters have the following characters:—

|                       | Boiling point<br>at 7mm. | Specific<br>gravity. | Optical<br>rotation. |
|-----------------------|--------------------------|----------------------|----------------------|
| Geranyl tiglate . . . | 149–151°                 | 0.9279               | $\pm 0^\circ$        |
| Citronellyl „ . . .   | 144–145°                 | 0.909                | $+2^\circ 6'$        |
| Phenylethyl „ . . .   | 139–140°                 | 1.0257               | $\pm 0^\circ$        |

**TILLEUL.**—See “Lime (or Linden) Blossom.”

**TILAM WANGI.**—See “Patchouli, Oil of.”

## P E R F U M E R Y

**TODDALIA, ACULEATA, OIL OF.**—*Toddalia aculeata*, (*T. asiatica*) is a tree growing wild in the Nilgiri mountains, and is also plentiful in the Philippine Islands.

Steam distillation of the leaves yielded 0.08 per cent. of an oil having a strong odour resembling a mixture of camphor and lemongrass. D. Hooper describes the oil distilled from the leaves of this species as having a pleasant odour resembling verbena or basilicum. The oil prepared by Brooks from material which was identified by Mr. Elmer D. Merrill, Chief of the Division of Botany of the Bureau of Science in Manila, possessed a strong odour, as mentioned above, and on freezing at  $-15^{\circ}$  a yield of 18 per cent. of a very volatile, unstable crystalline solid which melted, after recrystallising from ligroin, at  $96.5^{\circ}$  to  $97^{\circ}$ . It had a strong camphor-like odour, but it was quite unstable. A sample carefully purified for combustion analysis changed, in twenty-four hours, to a mass of oil and crystals.

The oil has a specific gravity about 0.906 at  $30^{\circ}$  and refractive index 1.4620 at  $30^{\circ}$ .

**TO-KO OIL.**—The Chinese plant, known locally as To-ko, is the herb *Asarum Blumei*. It yields 1.4 per cent. of essential oil of a yellow colour, having an odour resembling sassafras. It has a specific gravity 1.0788, and specific rotation  $+5^{\circ} 3'$ . It contains safrol, eugenol, and a terpene.

**TOHN.**—See "Balsam of Tolu."

**TONKIN BEANS.**—See "Dipteryx."

**TONQUINOL.**—This is a fancy name for some type of artificial musk, or a mixture of several of them, or of the residues resulting from their preparation.

**TRAMATES SUAVEOLENS.**—This plant is a fungus, growing principally on willow trees. It has a pleasant odour recalling that of aniseed, but the odorous substance appears to be destroyed on heating with water, so that no essential oil has been obtained.

**TRAWAS OIL.**—See "Litsea Oil."

**TREDECYL ALDEHYDE.**—This body resembles tetradecyl aldehyde in its general characters, but has a slightly less powerful and persistent odour. The normal aldehyde has the formula  $\text{CH}_3(\text{CH}_2)_{11}\text{CHO}$ . The isomer  $\beta$ -methyl-duodecyl aldehyde  $\text{CH}_3$

$(\text{CH}_2)_8\text{CH}(\text{CH}_3)\text{CH}_2\cdot\text{CHO}$  is prepared in a similar manner to tetradecyl aldehyde, by the condensation of methyl-nonyl ketone with bromoacetic ester, dehydration of the hydroxy ester, reduction to methyl duodecyl alcohol, and dehydrogenation of this to the aldehyde. (See "Tetradecyl Aldehyde.")

**TRÈFLE.**—No perfumes sold under the name of Trèfle are, in fact, the product of any species of *Trifolium*. *Trifolium pratense* (natural order *Leguminosæ*) is the common red clover of the meadow, and is grown chiefly for pasture. There are several odorous species, of which the best known is *Trifolium incarnatum*, the carnation or scarlet clover, whose odour has given the name to perfumes devoid of any of the scent of the actual flower. *Trifolium odoratum* is another odorous species, and is a native of Italy.

Perfumes bearing the name "Trèfle" are almost invariably based on a large proportion of amyl salicylate, which is also used in artificial orchid perfumes. Isobutyl salicylate is also used, and numerous other artificial and natural perfumes are employed to give the perfume any desired note. Amongst these are phenyl-acetic acid, vanillin, benzylidene acetone, jonquil, ylang-ylang, tuberose, and jasmin.

The flowers of *Trifolium incarnatum* have been distilled by Rogerson (*Jour. Chem. Soc.*, 1910, **97**, 1004), who obtained 0.029 per cent. of a pale yellow oil, calculated on the dried clover, which had a specific gravity 0.9597 at  $\frac{20^\circ}{20^\circ}$ , optical rotation,  $-1^\circ 48'$ , and boiled between  $120^\circ$  and  $180^\circ$  at 15 mm. Power and Salway (*Jour. Chem. Soc.*, 1910, **97**, 232) obtained 0.028 per cent., calculated on the dry flowers, of essential oil having a specific gravity 0.9476 at  $\frac{20^\circ}{20^\circ}$  and optical rotation  $+4^\circ 10'$ .

**TRENTEPOHLIA JOLITHUS.**—This plant is an Alga belonging to the family *Chroolepidaceæ*. It possesses an odour of violets. It is known in Germany, where it is found covering the rocks of the Riesengebirge with a grey-green coating, as *Reichenmoss* (violet moss). On distillation it yields a small quantity of essential oil with a violet-like odour.

**TRIACETIN.**—See "Glyceryl Triacetate."

**TRIETHYL CITRATE.**—The triethyl ester of citric acid, commonly known as ethyl citrate, is an ester prepared artificially,

## P E R F U M E R Y

and is used as an adulterant of essential oils containing esters. (See "Artificial Esters.")

**TRIMETHYL-HEXANONE.**—Trimethyl-hexanone,  $C_9H_{18}O$ , is a ketone which Masson (*Comptes Rendus*, 1912, 154, 517) has isolated from oil of labdanum. It is an odorous oil having the following characters —

|                                  |               |
|----------------------------------|---------------|
| Boiling point . . . . .          | 178°–179°     |
| Specific gravity at 0° . . . . . | 0.922         |
| Optical rotation . . . . .       | $\pm D^\circ$ |
| Refractive index . . . . .       | 1.4494 at 23° |

**TRINITRO-BUTYL-XYLENE.**—See "Musk, Artificial."

**TUBERONE.**—Verley (*Bull. Soc. Chim.*, 1899, iii, 21, 307) claimed to have isolated a ketone of the formula from  $C_{13}H_{20}O$  from oil of tuberose to which he gave the name tuberone. The presence of this body has not been confirmed by other workers on the oil.

**TUBEROSE, OIL OF.**—See "*Polianthes Tuberosa*."

**TULIP.**—No tulip perfume is extracted commercially, and it is only occasionally that artificial tulip perfume is met with. This, however, is of a fancy character and has practically no relationship with the perfume of the flower. The only tulip having any marked perfume is *Tulipa suaveolens*, the sweet tulip. It has a perfume recalling that of the *Marchal Niel* rose.

**TURPENTINE, OIL OF.**—It is true that oil of turpentine, as such, has no interest to the perfumer, but as, from a secondary point of view, it concerns the perfume industry very closely, inasmuch as it is the raw material for such substances as terpineol and camphor, and has been used to a considerable extent as an adulterant of essential oils, an account of its properties will be of interest.

The exudation from the wood of various members of the *Coniferae* is an oleo resin consisting of a mixture of resin and a volatile oil. This mixture is "crude turpentine," and when the essential oil is distilled off, the residue is common resin or colophony and the oil is known as oil of turpentine, or more commonly as "turpentine."

The principal sources of American turpentine are the so-called long-leaved pine, *Pinus palustris* (*Pinus australis*), *Pinus heterophylla*, and, to some extent, *Pinus echinata*. There are, however,

numerous other pines which yield turpentine in the United States. French turpentine is obtained principally from *Pinus pinaster* (*Pinus maritima*). Russian turpentine is the product of *Pinus sylvestris*, *Pinus Ledebourii*, and other species. Italian turpentine comes chiefly from *Pinus picca* and *Pinus pinaster*. Greek turpentine is obtained from *Pinus halepensis*, and Indian turpentine is produced from *Pinus longifolia*.

The methods by which the turpentine is extracted from the trees vary in different countries. In the United States the oleoresin is collected by what is known as the box system, or by the cup and gutter system. The box system involves making incisions across the trunk of the tree which are inclined inwards and terminate in a hollow excavation, or "box," about 12 to 18 inches above the ground level. The oleoresin flows into this box, and is baled out from time to time, and fresh incisions leading to the box are made. In the cup and gutter system the oleoresin flowing from the wound in the tree runs through "gutters," or strips of galvanised iron, into earthenware pots or cups suspended below. For the methods by which the French turpentine is collected, reference may be made to an article by Veze (Roure-Bertrand *Fils Bulletin*, 1909, 2, 9, 3). Briefly, it is as follows. The crude oleoresin or *gomme*, as it is called, exudes from an incision made by the axe of the collector in the stem of the pine. Kept open by the removal of a thin slice every week, this incision, the *carre* as it is called, rises gradually up the trunk of the tree until it reaches, after five years' working, a height of nearly 4 metres. The tree is then left alone for two or three years, after which a fresh *carre* is made at another point of the base. The same tree is tapped in this manner for about forty years, when it is bled to death by several *carres* made simultaneously, and is then felled for timber. From the top of the *carre* the drops of oleoresin exude and run down into a vessel placed to receive them, which consists of an earthenware or metal pot. In India the method is similar to and based on the French method; the trees are subject to light tapping or to heavy tapping, according to the approximate time before the trees are due to be felled. If the trees are not to be felled for more than five years ahead, light tapping is resorted to, and only a moderate number of incisions or "blazes" are made. But if the trees are due to be felled within five years, they are "tapped to death" with as many blazes as there is room for. In the case of light tapping, it is customary in India to tap for a certain number of

## PERFUMERY

years, and then to allow a period of rest, before tapping is recommenced. In the Naini Tal Division, and in Kumaon generally, the rule hitherto has been to tap for five years, and then to give a rest of ten years, fifteen years being the "tapping cycle." In other divisions a nine-year tapping cycle (three years' tapping and six years' rest) has been common. As a result of general experience, a twelve years' cycle (four years' tapping and eight years' rest) appears to be the most advantageous. (See "Indian Forest Memoirs" (Sylviculture Series), vol i, pt i, p. 100.)

**American Turpentine.**—The principal adulterant of normal turpentine oil in the United States is the so-called *wood turpentine* or *stump turpentine*. This is a turpentine oil obtained by distilling the cut pine, fir, and spruce wood in closed retorts, and as the best qualities are distilled with steam, the product obviously does not differ to a very great extent from the ordinary exudation turpentine. But as the stumps from which the oil is obtained have generally been allowed to remain in the ground for several years after the trees have been felled, the conditions of formation of the oil are not identical with those obtaining when the trees were in full growth and performing their normal physiological functions, and a difference in the composition of the oil is to be expected. The following account of the adulteration, analysis, and standards of American turpentine oil by the writer (E. J. Parry) are reproduced from *The Chemist and Druggist*, August 24th, 1912:—

"The use of petroleum products as adulterants is, as is well known, one of the commoner forms of sophistication, but fortunately this presents little difficulty to the analyst, on account of the wide difference in characters between the terpenes and the hydrocarbons found in petroleum products. The adulteration, however, which is giving most trouble at present is the use of so-called 'wood' or 'stump' turpentine, which resembles the ordinary or 'gum' turpentine so closely, especially when well rectified, as to make its detection far more difficult than is the case with petroleum products. The United States Department of Agriculture last year issued suggested standards for pure turpentine, of which that for No. 1 or 'standard' turpentine is the only one which need be referred to here. The suggested standards are as follows: specific gravity at 20° = 0.862 to 0.870; refractive index at 20° = 1.4680 to 1.4760; 95 per cent. should distil below 170°. On polymerisation with sulphuric acid (thirty-eight times normal), the residue should not exceed 1 per



## PERFUMERY

\*cent., and should have a refractive index of 1.500 to 1.520. I have no particular objection to take to these figures, other than to say that a considerable amount of stump turpentine may be present in an oil complying with them.

"The close similarity in physical characters between pure gum turpentine and the so-called stump turpentine, therefore, renders it necessary that some further distinctive features shall, if possible, be taken into account, and the result of the examination of a very large number of pure and adulterated samples leads me to consider that the behaviour of the oil towards the halogen elements gives the most useful indications of admixture with wood or stump turpentine—which, by the way, must be so described in America, where it is not allowed to be dealt in as "turpentine" without proper qualification.

"Both the iodine and the bromine values have been recommended in this respect, but the iodine value is, in my opinion, the more useful of the two. Its value depends on the fact that the hydrocarbons present in wood turpentine—probably on account of the method of treatment adopted in its manufacture—appear to be more saturated than those present in normal turpentine, and therefore absorb less iodine to form a fully saturated compound.

- "The iodine value may be determined by either the Wijs or the Hubl method, and it is necessary that the method used should be stated and the conditions of the determination kept constant. Useful indications are given by the determination of the iodine value of the 10 per cent. left after distillation of 90 per cent. of the sample, since the highly unsaturated hydrocarbons appear to concentrate in the higher boiling fractions. The following processes may be used for the determination of the bromine value: (1) One cubic centimetre of the oil is dissolved in 5 c.c. of chloroform, and a 3 per cent. aqueous solution of bromine added with shaking until a permanent coloration remains; the strength of the bromine solution is determined in the usual manner, and the amount combining with the oil can be calculated. (2) One cubic centimetre of the oil is dissolved in 50 c.c. of absolute alcohol, and 5 c.c. of hydrochloric acid added. A solution of 28 grams of bromate of potassium and 100 grams of bromide of potassium per litre is then added until a permanent brown colour remains for one minute after well shaking. The bromine absorbed is calculated for 1 c.c., which can be reduced to the proper bromine number by dividing it by the specific gravity, say, 0.86. So far as my

## P E R F U M E R Y

experience goes, the following figures would form satisfactory standards for genuine American turpentine :—

|   |                              |
|---|------------------------------|
| Specific gravity at 15.5°                             | 0.862-0.870                  |
| Refractive index at 20°                               | 1.4680-1.4730                |
| Initial boiling point                                 | Not below 154°-155°          |
| Distillate under 160°                                 | 72-73 per cent.              |
| "          "      170°                                | 95-97                        |
| Bromine value   | Not below 1.9                |
| Iodine value (Hubl, 16 hours)                         | 360-375                      |
| "          "      (Wijs, 1 hour)                      | 335-350                      |
| "          "      of last 10 per cent. (Wijs, 1 hour) | Not less than 350            |
| Iodine value of last 10 per cent. (Hubl, 16 hours)    | "          "      "      350 |

The iodine figures may require a little modification as one's experience becomes more enlarged in this direction.

"I think that the examination of the refractive index of the higher boiling fractions may afford valuable information, but hesitate to give any figures until experience in this direction is somewhat wider than it is at present. The value of the iodine figures is indicated by the fact that wood or stump turpentine will often show an absorption of from 230 to 300, and the last 10 per cent an absorption of about the same figure, or even less. I have made a careful examination of the numerous colour reactions proposed for the testing of this oil, and I can say emphatically that none of them is of the least use, and cannot be relied upon when one is dealing with the rectified variety of wood turpentine, although some of them are useful in dealing with the crude variety. But, as the highly rectified variety is always used for admixture with ordinary turpentine, the tests in question are invariably useless

"Dealing briefly with the question of adulteration with petroleum products, I would point out that it is a practical impossibility for any turpentine adulterated with petroleum of any kind to comply with the above-mentioned requirements. But if it is necessary to examine a given sample with a view to showing to what extent an oil is so adulterated, the following process will give excellent results. It is a modification of Armstrong's polymerisation process due to Eibner and Hue (*Chem. Zeit.*, 1910, 643). . . .

"Fifteen cubic centimetres of concentrated sulphuric acid (specific gravity 1.84) are introduced into a suitable shaking burette,

# P E R F U M E R Y

and 10 c.c. of the oil added in quantities of 0.5 c.c. at a time, with constant shaking. From fifteen minutes to one hour will be required for this operation, according to the amount of petroleum present. After the addition of the oil is complete, the burette is thoroughly shaken and sulphuric acid run into the burette until the latter is nearly full. After six hours the amount of oil rising to the surface is read off. If this does not exceed 2 c.c., the oil is probably pure. The polymerised products are now run off and treated with from 2 to 4 volumes of fuming sulphuric acid, and well shaken in a fresh burette. The ultimate residue should not exceed 0.3 per cent. if the oil is free from petroleum. Further, if the oil be free from the usual adulterants, this unpolymerised residue will have a refractive index of not less than 1.500, and not more than 1.520.

"The following table contains the figures for pure American turpentine, and for a number of samples adulterated by myself with known quantities of given adulterants, and also of a few samples of adulterants themselves:—

|   | (1)<br>Pure<br>American<br>turpen-<br>tine. | (2)<br>Wood<br>turpen-<br>tine. | (3)<br>50 per<br>cent. each<br>(1) and (2) | (4)<br>"Petro-<br>leum"<br>turpen-<br>tine. | (5)<br>50 per<br>cent. each<br>(1) and (4). |
|---|---|---------------------------------|--|---|---|
| Specific gravity . . . . .                            | 0.866                                       | 0.873                           | 0.869                                      | 0.808                                       | 0.838                                       |
| Refractive index . . . . .                            | 1.4720                                      | 1.4745                          | 1.4737                                     | 1.4490                                      | 1.4610                                      |
| Initial boiling point . . . .                         | 155°  | 159°                            | 157°                                       | 98°   | 99°   |
| Distillate under 160° . . . .                         | 74 per<br>cent.                             | 61 per<br>cent.                 | 68 per<br>cent.                            | 48 per<br>cent.                             | 62 per<br>cent.                             |
| "    "    170° . . . . .                              | 94 per<br>cent.                             | 78 per<br>cent.                 | 84 per<br>cent.                            | 75 per<br>cent.                             | 82 per<br>cent.                             |
| Bromine value . . . . .                               | 2.2   | 1.46                            | 1.82                                       | 0.05  | 1.1   |
| Iodine value (Hübl) . . . . .                         | 372   | 264                             | 321  | 9.0   | 190.5                                       |
| "    "    (Wijs) . . . . .                            | 350   | 240                             | 298  | 8.4   | 179   |
| "    "    of last 10 per cent.<br>(Hübl) . . . . .    | 360   | 251                             | 304  | 9.0   | 184   |
| Iodine value of last 10 per cent.<br>(Wijs) . . . . . | 355   | 242                             | 298  | 8.5   | 177   |
| Refractive index of—                                  |   |                                 |  |   |   |
| First 20 per cent. . . . .                            | 1.4719                                      | 1.4731                          | 1.4728                                     | 1.448                                       | 1.4660                                      |
| Second " . . . . .                                    | 1.4700                                      | 1.4730                          | 1.4720                                     | 1.449                                       | 1.4675                                      |
| Third " . . . . .                                     | 1.4712                                      | 1.4734                          | 1.4722                                     | 1.4481                                      | 1.4721                                      |
| Fourth " . . . . .                                    | 1.4712                                      | 1.4732                          | 1.4721                                     | 1.4470                                      | 1.4721                                      |
| Fifth " . . . . .                                     | 1.4781                                      | 1.4842                          | 1.4821                                     | 1.4495                                      | 1.4735                                      |

Corresponding figures for a large number of pure American

*PERFUMERY*

turpentines showed the following limit values for a large number of samples :—

|                                       |                   |
|---------------------------------------|-------------------|
| Specific gravity at 15°               | 0.862-0.870       |
| Refractive index                      | 1.4680-1.4730     |
| Initial boiling point                 | 154°-155.5°       |
| Distillate under 160°                 | 72-74.5 per cent. |
| "    "    170°                        | 95-97.5    "      |
| Bromine value                         | 1.96-2.31         |
| Iodine value (Hübl)                   | 360-375           |
| "    "    (Wij)                       | 335-350           |
| "    "    of last 10 per cent. (Hübl) | 349-369           |
| "    "    "    "    (Wij)             | 350-365           |
| Refractive index of—                  |                   |
| First 20 per cent                     | 1.4700-1.4722     |
| Second    "    "                      | 1.4700-1.4724     |
| Third    "    "                       | 1.4710-1.4735     |
| Fourth    "    "                      | 1.4710-1.4740     |
| Fifth    "    "                       | 1.4780-1.4821     |

(See also E. J. Parry, "The Chemistry of Essential Oils," 4th ed., vol. i., pp. 9-32.)

According to Schkatelow (*Moniteur Scientifique*, 1908, iv., 22, i., 217), the following trees yield oleoresins, the turpentine of which have the characters given.—

|                         | Yield per cent. | Optical rotation. | Specific gravity. |
|-------------------------|-----------------|-------------------|-------------------|
| <i>Pinus sylvestris</i> | 15-16           | + 22° to + 24°    | 0.867 at 15°      |
| <i>Abies excelsa</i>    | 13.4            | — 132°            | 0.873 at 15°      |
| <i>Larix sibirica</i>   | 14.1            | — 14.3°           | 0.870 at 19°      |
| <i>Pinus cembra</i>     | 6               | + 14.04°          | 0.865 at 15°      |
| „ <i>taurica</i>        | 20              | — 75.9°           | 0.861 at 19°      |
| <i>Abies sibirica</i>   | 28              | — 35.6°           | 0.875 at 19°      |

The following details in reference to commercial Russian oil of turpentine are by the writer (E. J. Parry), and are reproduced from the *Chemist and Druggist*, October 26th, 1912:—

“During the past twelve months I have had occasion to examine a large number of samples of Russian turpentine. In view of the results I have obtained, it will be useful to quote the text-book statements in reference to this oil. The writer (*‘Chemistry of Essential Oils,’* 2nd ed., p. 149) states that ‘its specific gravity is usually about 0.870 to 0.875, and its boiling point about 170°. It is dextrorotatory to the extent of + 20°.’ Allen (*‘Commercial Organic Analysis,’* 1911, iv., p. 401) states:—

## P E R F U M E R Y

“A sample of Russian turpentine oil of specific gravity 0.8682 examined by W. A. Tilden was found to contain from 10 to 15 per cent. of a pinene boiling at about the same temperature as australene, but having the specific rotation of 23.5°; 60 to 70 per cent. of sylvestrene; a considerable quantity of cymene; and small proportions of viscid hydrocarbons boiling at high temperatures.’ ‘The specific gravity of the Russian oil of commerce ranges from 0.8620 to 0.8722’ (p. 412). ‘Russian turpentine oil distils chiefly between 165° and 190°’ (p. 413).

“The following figures, communicated by L. Archbutt, also show the behaviour of samples of turpentine oil, believed to be genuine, when distilled under the conditions described :—

### *Russian Oil*

| Distillate from 100 c.c. | Range of temperature. | No. of samples. |
|--------------------------|-----------------------|-----------------|
| 1 c.c.                   | 161.1°–164.5°         | 4               |
| 5 c.c.                   | 163.9°–169.4°         | 8               |
| 90 c.c.                  | 177.2°–188.9°         | 8               |
| 95 c.c.                  | 181.7°–215.5°         | 8               |
| *96.5–98 c.c.            | 187.8°–208.9°         | 7               |

For some time past I have suspected that Russian turpentine, as known in this country, is not a natural product at all, but that it is a fractionated oil from which a good deal of the ‘middle runnings’ have been removed. This belief has been amply confirmed by Professor Schindelmeyer, of Dorpat University, who tells me that we never see natural or ‘virgin’ Russian turpentine in this country. The oil is fractionated, and the portions boiling at about the same temperature as American turpentine are largely removed, and are used in Russia for industrial purposes, the low and high boiling fractions being then mixed and exported as Russian turpentine. He has also placed authentic samples at my disposal, informing me that normal Russian turpentine contains from 40 to 70 per cent. distilling from 155° to 160°, and consisting chiefly of pinene.

“The Russian turpentine arriving in this country is of an entirely different character, and even when accepted as more or less satisfactory, on the principle that it is the best one can get, it frequently arrives in a condition which buyers refuse to recognise as of good merchantable quality. The following figures are those

# PERFUMERY

of a number of the best available Russian turpentine on the London market, and which are, subject to some reserve, accepted as satisfactory.—

|                            | 1          | 2          | 3          | 4.          |
|----------------------------|------------|------------|------------|-------------|
| Initial boiling point      | 157°       | 156°       | 157°       | 158°        |
| Distils below 155°         | None       | None       | None       | None        |
| „ 155°-160°                | 1 per cent | 1 per cent | 5 per cent | 11 per cent |
| „ 160°-165°                | 44         | 45         | 40         | 18          |
| „ 165°-170°                | 37         | 35         | 42         | 48          |
| „ 170°-180°                | 15         | 16         | 10         | 19          |
| „ above 180°               | 3          | 3          | 3          | 4           |
| Specific gravity at 15°    | 0.863      | 0.8635     | 0.863      | 0.868       |
| Refractive index at 20°    | 1.4730     | 1.4726     | 1.4725     | 1.4748      |
| Optical rotation           | + 4° 28'   | + 4° 30'   | + 9°       | + 8°        |
| Absorbed by 5 per cent KOH | Nil        | Nil        | Nil        | Nil         |

A very large number of samples, however, have been even more largely deprived of their middle runnings, and contain a considerable amount of hydrocarbons boiling over 180°, and also a considerable amount of acid bodies, which are absorbed by caustic potash. Such samples are quite useless to the rectifier, as their redistillation must ensure the removal of the acid bodies, and also of the bodies boiling over 180°, with a resulting loss which causes the rectification to be unremunerative.

“The following are typical samples of this character, of which I have examined a very large number recently —

|                         | 1          | 2            | 3            | 4           |
|-------------------------|------------|--------------|--------------|-------------|
| Initial boiling point   | 148°       | 116          | 146°         | 153°        |
| Distils below 155°      | 2 per cent | 3 per cent   | 5.5 per cent | 1 per cent  |
| „ 155°-160°             | 3          | 3            | 5            | 3           |
| „ 160°-165°             |            |              |              |             |
| „ 165°-170°             | 35         | 34           | 22           | 36          |
| „ 170°-180°             | 18         | 50           | 46           | 50          |
| „ above 180°            | 12         | 10           | 21.5         | 40          |
| Specific gravity at 15° | 0.868      | 0.8665       | 0.878        | 0.869       |
| Refractive index at 20° | 1.4762     | 1.4756       | 1.4780       | 1.4792      |
| Optical rotation        | + 8°       | + 9°         | + 11°        | + 12° 45'   |
| Absorbed by KOH         | 6 per cent | 8.5 per cent | 7 per cent   | 3 per cent. |

Sample No. 3 is a particularly bad one, the high specific gravity

corresponding with the high refractive index and the large amount distilling above 180°.

"Where Russian turpentine is used for the purpose of, for example, the manufacture of disinfectants of the Sanitas type, it is probably not of nearly so much importance that it should contain a very high amount of hydrocarbons boiling at a comparatively low temperature; but where it is used for the purposes of rectification so as to, as far as possible, remove the odour in order that it may be used for the manufacture of paints and varnishes, the distillation figures are of the highest importance, and it is only samples that comply with certain requirements that are remunerative for distillation purposes.

"Assuming that the type of oil of the best quality that has been seen on the London market for some years, and which is, and has been for some time, accepted as of good merchantable quality, is to be understood as Russian turpentine, then, in my opinion, the following figures would be fair standards to work upon:—

|  |                           |
|--|---------------------------|
| Specific gravity at 15°                            | 0.862–0.872               |
| Optical rotation                                   | + 3° to + 20°             |
| Refractive index at 20°                            | 1.4700–1.4750             |
| Absorbed by 5 per cent.<br>caustic potash solution | Not more than 3 per cent. |
| Distils below 155° °.                              | Not more than 1    "      |
| "      170°  | Not less than 75    "     |
| "      180°  | Not less than 95    "     |

As mentioned above, Professor Schindelmeyer informs me that he has never met with a pure virgin Russian turpentine containing less than 40 per cent. of hydrocarbons distilling between 155° and 160°. I cannot say of my own knowledge if this figure is a proper

|                             | 1.          | 2.           |
|-----------------------------|-------------|--------------|
| Specific gravity            | 0.867       | 0.865        |
| Optical rotation            | + 7° 50'    | + 10°        |
| Refractive index            | 1.4718      | 1.4736       |
| Absorbed by 5 per cent. KOH | 5 per cent  | 6 per cent   |
| Distilled below 155°        | Traces only | Traces only  |
| "      155°–160°            | 65 per cent | 63 per cent. |
| "      160°–165°            | 11    "     | 9    "       |
| "      165°–170°            | 13    "     | 15    "      |
| "      170°–180°            | 7.5   "     | 7    "       |
| "      above 180°           | 3.5   "     | 6    "       |

## P E R F U M E R Y

minimum limit for virgin Russian turpentine, but those samples of known authenticity which I have examined certainly contained more than 40 per cent of such hydrocarbons

"The two samples shown in table on p 777 are typical virgin crude Russian turpentine

"From these two samples the tarry and acid bodies were removed and the rectified sample in the case of No 1, had the following characters —

|                   |             |
|-------------------|-------------|
| Specific gravity  | 0.8646      |
| Optical rotation  | + 8°        |
| Refractive index  | 1.4890      |
| Absorbed by KOH   | None        |
| Distils below 155 | None        |
| 155°-160          | 68 per cent |
| 160°-165          | 13          |
| 165°-170          | 10          |
| 170-180           | 7           |
| above 180         | 2           |

It is, therefore, obvious that the whole question of Russian turpentine requires careful consideration, as the oil as it now comes into the London market varies very considerably even if it comes within the description of 'good merchantable quality' "

French turpentine oil is usually highly dextrorotatory. Most samples will be found to have characters falling within the following limits —

|                      |                |
|----------------------|----------------|
| Specific gravity     | 0.862-0.874    |
| Optical rotation     | 20° to - 40°   |
| Boiling point        | 153°-154°      |
| Distillate below 160 | 50-90 per cent |

Greek turpentine has the following characters —

|                  |               |
|------------------|---------------|
| Specific gravity | 0.860-0.866   |
| Optical rotation | + 34 to + 48° |
| Refractive index | 1.4670-1.4745 |
| Boiling point    | 153°-154°     |

Indian turpentine has a higher boiling point than American and most European oils. Its specific gravity is 0.865 to 0.875, optical rotation 0° to + 4°, and initial boiling point, 165°.

The principal constituent of most turpentines is the terpene pinene, associated with more or less of other terpenes, which vary according to the source of the oil. (For the details of the composition of the various turpentines, see "The Chemistry of Essential Oils," *loc cit*.)

**UMBELLIFERONE.**—This body is the lactone of umbelliferone



## P E R F U M E R Y

acid (2:4-dihydroxy-cinnamic acid), and is identical with 4-hydroxycoumarin. German camomile oil (from *Matricaria Chamomilla*) contains a substance melting at 110° and having, when dissolved in sulphuric acid, a blue fluorescence. It appears to be the methyl ether of umbelliferone. Umbelliferone also occurs in the essential oil of *Laretia acaulis*.

**UMBELLULARIA CALIFORNICA.**—See “Californian Bay.”

**UMBELLULONE.**—This body is a ketone isolated from the oil of Californian bay, *Umbellularia Californica*, by Power and Lees. It is a saturated compound, of the formula  $C_{10}H_{14}O$ , having an odour resembling that of mint. It is a liquid having the following characters:—

|                            |                 |
|----------------------------|-----------------|
| Specific gravity . . . . . | 0.950 at 20°    |
| Optical rotation . . . . . | — 36° 30'       |
| Refractive index . . . . . | 1.48325         |
| Boiling point . . . . .    | 220° at 749 mm. |

It forms a semicarbazone melting at 240° to 243°.

**UNCINEOL.**—Baker and Smith (*Jour. and Proc. Roy. Soc. N.S.W.*, 1907, 41, 196) isolated this alcohol, of the formula  $C_{10}H_{18}O$ , from the essential oil of the leaves of *Melaleuca uncinata*. It forms fine white crystals melting at 72° to 73°, and has a specific rotation + 37°.

**UNDECINE CARBONATES.**—See “Heptine Carbonates.”

**UNDECYLENIC ALCOHOL.** This alcohol is an unsaturated compound of the formula  $CH_2:CH(CH_2)_8CH_2OH$ . It is a liquid, boiling at 128° at 13 mm. pressure. On cooling to about - 20°, it solidifies, and then melts at 12°. It occurs in the essential oil of the leaves of *Litsea odorifera* (oil of trawas), and is manufactured artificially. It is used in minute quantities only. Its specific gravity is about 0.854.

**UNDECYLENIC ALDEHYDE.**—This body, of the formula  $CH_2:CH(CH_2)_8CHO$ , is one of the unsaturated higher fatty aldehydes. It is of use in modifying floral odours, but must be employed in minute amounts. It melts at + 5° to + 7°, and boils at 113° at 13 mm.

**UNDECYLIC ALCOHOL.**—This alcohol (methyl-nonyl-carbinol) has the constitution  $CH_3(CH_2)_7CH_2CH(CH_3)OH$ . It has been found in Algerian oil of rue, and in the oil of the leaves of *Litsea odorifera*. It has an intense odour. It boils at 231° to 233°.

and has an optical rotation  $-5^{\circ} 12'$ , specific gravity 0.839, and refractive index 1.440. On oxidation it yields methyl-nonyl ketone, which forms an oxime melting at  $46^{\circ}$ , and a semicarbazone melting at  $124^{\circ}$ .

**UNDECYLIC ALDEHYDE.**—This aldehyde, of the formula  $\text{CH}_3(\text{CH}_2)_9\text{CHO}$ , is one of considerable value to perfumers, and is used in the modification of floral odours for the production of proprietary perfumes. The following method is used for its production (Lewinsolin, *P. & E. O. R.*, 1924, 79):—

Cocoanut fat contains palmitic, myristic, and especially lauric acids in the form of their glycerides. In addition to these acids, the hydrolysis of cocoanut fat yields small quantities of capronic acid (0.2 per cent.), caprylic acid (3.3 per cent.), and capric acid (0.4 per cent.). For the separation of these different aliphatic acids advantage is taken of the method of "alcoholysis" devised by Haller (*Bull. Soc. Chim.*, 1907, p. 649). The fat is warmed with twice its weight of methyl alcohol in which 1 to 2 per cent. of HCl gas has been dissolved. After two hours on the boiling-water bath, the excess methyl alcohol is distilled off, the residue neutralised with sodium bicarbonate, and fractionated *in vacuo*, when the following fractions are obtained:—

1.  $95^{\circ}$  to  $147^{\circ}$  at 18 mm., methyl esters of capronic, caprylic, and capric acids.

2.  $148^{\circ}$  to  $159^{\circ}$  at 18 mm., methyl laurate (about 65 per cent.).

3.  $160^{\circ}$  to  $200^{\circ}$  at 18 mm., methyl myristate and palmitate.

**Hydrolysis of Lauric Ester.**—Three kilograms of methyl laurate are heated under a reflux condenser with a solution of 780 grams of KOH dissolved in a suitable quantity of 95 per cent. alcohol. After the hydrolysis, 3 litres of water are added, and the liquid acidified with dilute sulphuric acid. The still liquid lauric acid (melted by the heat of neutralisation of the alkali) is separated from the aqueous layer, and weighs about 2.240 kg. It is dissolved in twice its weight of chloroform and dried over anhydrous sodium sulphate.

**Conversion into Acid Chloride.**—The chloroform solution of the acid is allowed to flow slowly into a well enamelled 20-litre vessel containing 3.480 g. of phosphorus pentachloride, which is warmed during the addition of the solution, and for two to three hours longer on the water bath. The HCl fumes are disposed of in the usual way. After the lapse of three hours the contents of the vessel are filtered through glass wool and rectified, the receiver being cooled in ice for the first runnings. After the chloroform (boiling

## P E R F U M E R Y

point  $61^{\circ}$ ) and the  $\text{POCl}_3$  (boiling point  $110^{\circ}$ ) have distilled, a vacuum water pump is attached and the distillation continued at low pressure. Lauryl chloride comes over at  $135^{\circ}$  to  $140^{\circ}$  at 10 mm., the yield being 2.320 kg.

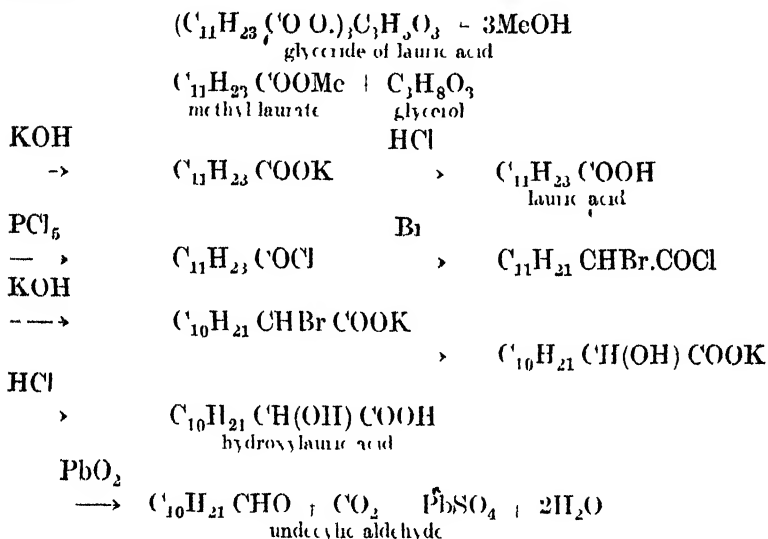
*$\alpha$ -Bromolauric Acid.*—To 2.320 kg. of lauryl chloride in an apparatus such as is used for the preparation of bromoacetic acid (see *P. & E. O. R.*, February, 1924, p. 44) are added slowly from a dropping funnel 2.200 kg. (i.e., 735 c.c.) of bromine. The bromination requires twelve to fifteen hours at the temperature of the water bath, after which time the product is diluted with 3 to 4 litres of water, shaking constantly and warming on the water bath to hydrolyse the bromolauryl chloride. The whole is then cooled, and the precipitated acid is washed twice with water, then with bisulphite solution, in order to remove traces of bromine, and finally dissolved in ether. The ether solution is washed with water and dried over anhydrous sodium sulphate; after removal of the ether (the last traces by means of a vacuum pump), the bromolauric acid is allowed to set in an enamelled dish. Yield, about 2.900 kg.

*$\alpha$ -Hydroxylauric Acid.*—In a 30-litre vessel of tinned iron the 2.900 kg. of bromolauric acid are boiled for three hours with a solution of 1.820 kg. of KOH in 20 litres of water. The cooled product is acidified with hydrochloric acid and  $\alpha$ -hydroxylauric acid is precipitated. A simple method for separating the hydroxy-acid from unchanged bromo acid is to dissolve the precipitate in warm chloroform. On cooling, the hydroxy-acid crystallises out quantitatively, while the bromo-acid remains in solution. Yield of hydroxylauric acid is about 2.150 kg, melting point  $73^{\circ}$  to  $74^{\circ}$ .

*Undecylic Aldehyde.*—The aldehyde is obtained by oxidation of hydroxylauric acid with lead peroxide. In a spacious flask, 2.150 kg. of hydroxylauric acid are treated with 2.150 kg. of lead peroxide and 8.600 kg. of 25 per cent. sulphuric acid, a strong current of steam being passed through the mixture. The undecylic aldehyde distils in the steam as a colourless oil. It is extracted from the distillate with ether, washed with water, dried, the ether removed, and the aldehyde rectified *in vacuo*. Undecylic aldehyde boils at  $116^{\circ}$  to  $117^{\circ}$  at 18 mm. It melts at  $-4^{\circ}$ , and has a specific gravity 0.830, and refractive index 1.4398. After a short time the aldehyde polymerises to a solid body, melting point  $46^{\circ}$  to  $47^{\circ}$ , boiling point  $125^{\circ}$  to  $126^{\circ}$  at 18 mm., and loses very appreciably in intensity of odour. On this account the aldehyde is put on the market in the form of its bisulphite compound, which

## P E R F U M E R Y .

is readily obtained by shaking the aldehyde with concentrated sodium bisulphite solution. From this compound the unpolymerised aldehyde is at any time recovered by the usual method of warming with dilute sodium carbonate solution. The yield of *n*-undecylic aldehyde is about 650 grams. The reactions involved in the preparation of undecylic aldehyde may be represented as follows —



The description of the methods of manufacture of the rarer aldehydes may be concluded with the remark that the 12-carbon aldehyde, *lauric* or *duodecyl aldehyde*, which is much esteemed in perfumery, may be prepared from the corresponding alcohol by dehydrogenation, as before described. In the same way, from myristic ester is obtained a normal aldehyde with fourteen carbon atoms, which possesses a pleasant peach smell. Palmitic ester gives an aldehyde with sixteen carbon atoms, having an intense odour of strawberries. Since all these aldehydes possess an intolerably intense odour, they find application, as already mentioned, only in 1 to 2 per cent solution.

**URENA LOBATA.**—The leaves of *Urena lobata*, which are known as *purpūṭ* in the Malay Peninsula, are used to adulterate the leaves of patchouli (*q v.*).

**USNEA.**—Various types of *Usnea*, one of the lichens, yield a valuable extract containing essential oil, and which is known as “mousse de chêne” (*q v.*)

•**VALERIAN, OIL OF.**—See “Nard.”

**VANILLA.**—The vanilla bean of commerce is a very important raw material of perfumery, and is produced on a very large scale. Its employment, however, is handicapped to some extent by the manufacture on an enormous scale of artificial vanillin. The odours of vanilla and vanillin are to be compared in the following manner. The principal odorous constituent of the vanilla bean is vanillin, which is present, as one of its natural ingredients. But there are other odorous substances present in vanilla beans which modify and round off the vanillin odour.

Artificial vanillin is absolutely identical with naturally occurring vanillin, and when both are absolutely pure their odours are identical. But artificial vanillin only reproduces that part of the odour of the bean which is due to the natural vanillin, so that the odour of the bean and of artificial vanillin are not identical. And the odour of the former is sweeter and softer than that of the latter, and vanillin must be regarded as a cheap but good substitute for the vanilla bean, and cannot be regarded as replacing it.

According to Ridley (“Spices,” Macmillan, 1912), vanilla was used by the Aztecs for flavouring chocolate before the discovery of America, and its use was adopted by the Spaniards. According to Morren, it was first brought to Europe in the early part of the sixteenth century, and described by Hernandez in 1651, in the “*Rerum Medicarum Novæ Hispaniæ Thesaurus*.” It was, states Ridley, introduced into England in the beginning of the nineteenth century by the Marquis of Blandford, and flowered and fruited in 1807. In 1812 plants from the gardens of the Right Hon. H. C. Greville were sent to Dr. Sonmé, Director of the Botanic Gardens of Antwerp, who in 1819 sent two plants to Buitenzorg, in Java, where one that had survived the voyage flowered in 1825, but did not fruit. Professor Morren, of Liège, was the first to produce fruits in quantity, and proved that *Vanilla planifolia* was the true vanilla of commerce. He indicated the method of fertilisation by hand, and suggested that vanilla might be readily cultivated in tropical countries. The cultivation of the plant was introduced into Java in a systematic manner by Teysmann in 1846. In 1850–1856 the cultivation was taken up in the island of Réunion, and thence to Mauritius. It was also cultivated in Tahiti, Fiji, Zanzibar, and Java.

Vanilla beans are the fruit, cured in various manners, of a climbing orchid of which many species exist, and many have been described as yielding the aromatic fruit. It is, however, clear

to-day that many of these are merely varieties of the same plant, and for all practical purposes it may be said that only two species are in cultivation. These are *Vanilla planifolia*, the true Mexican vanilla, having long slender pods, and *Vanilla pompona*, the West Indian vanilla, which has short thick pods, known as vanillons.

*Vanilla planifolia* is a vigorous climbing orchid, with long succulent green stems, from which twining white aerial roots emerge opposite the leaves, and by which the plant clings for support to trees, etc. It is a native of south-eastern Mexico, British Honduras, Costa Rica, and Guatemala, and has been introduced into most tropical countries.

*Vanilla pompona* resembles *Vanilla planifolia* generally in appearance, except that its leaves are larger, the flowers are larger and more fleshy, and the fruit is shorter and much thicker.

The flowers of vanilla, although hermaphrodite, have the stigma covered with a disc-like membrane which practically prevents natural pollination. And whilst it is true that in Mexico the flowers are sometimes fertilised by small bees belonging to the genus *Melipona*, and by small humming birds, artificial fertilisation is frequently resorted to. But, apart from Mexico, the flowers are either not visited by these insects, or, if they are, fertilisation does not result, so that hand fertilisation has to be resorted to. It is generally stated that this process is one of great skill and delicacy, but, as a matter of fact, women and children become quite proficient at it in the course of a few days' experience. A skilful operator can fertilise from 1,000 to 1,500 flowers in a morning. *Vanilla planifolia* flowers only once a year, generally from September to November, sometimes commencing as early as June. Early flowering, say, in March to May, is regarded as indicating an unhealthy condition of the plant. *Vanilla pompona*, on the other hand, usually gives two crops of flowers annually. The main season begins about the middle of July, and lasts until September. The second flowering usually commences early in the year, in January, and runs into February or March. Macfarlane has suggested that both species of vanilla should be cultivated on an estate, so that, as the flowering times are different, the work can proceed all the year round. According to Ridley, a strong vanilla plant in full vigour should produce up to 200 bunches of flowers at a time, each carrying fifteen to twenty flowers, so that 4,000 flowers may be obtained on a single plant. Only a certain number of these should be fertilised—possibly about one half—

## PERFUMERY

and when the fruits are growing the shorter ones are removed, leaving only about one-third as many fruits to develop as there were originally flowers on the vine. When it is desired to produce only the long beans, which fetch a higher price than the short ones, still more of the young fruits are removed.

The flowers, when they open, remain open for only one day, beginning to close at about three o'clock in the afternoon. The best time for hand fertilisation is from eight o'clock in the morning till one or two o'clock in the afternoon. The best effects are produced on a dry day, when it has been raining the previous day. The operator, usually a woman or child, takes the flower in the left hand and presses the lip down so as to expose the column, which is lightly held between the finger and thumb. In the right hand is held a small splinter of wood or bamboo, bluntly pointed at both ends, so that either end can be used. The cap of the anthers and the rostellum, which covers the stigma, are pushed up with this splinter, and by suitable pressure of the thumb and finger the anther cup rises, and the pollen is exposed and is removed by the point of the splinter and transferred to the stigma below the rostellum. The stigma, being sticky, retains the pollen, and the rostellum, being released, flies back to its original position and helps to press the pollen into the stigma. From a theoretical point of view, it is, of course, obvious that the transference of pollen from other flowers would be the better method, but in practice the risks of losing the pollen during transference between flower and flower would probably result in so considerable a proportion of failures that the contrary practice is adhered to. Generally speaking, 90 per cent of the flowers pollinated come to fruit with average skill, but it is necessary for the vanilla planter to keep a careful watch over the flowers in order to ensure that the operators are performing their work skilfully. If the flower has been fertilised, it rapidly withers, and the petals and sepals fall off, but if the operation has been unsuccessful, the column falls off with the petals. About a month after fertilisation, most planters—in Madagascar at all events—press a mark on the beans to guard against theft. It takes a period of from four to seven months for the beans to fully mature, the time depending on the weather. The fruit first becomes dark green and smooth, but turns to a yellowish colour when fully ripe. The pods or beans of *Vanilla planifolia* have a tendency to split during ripening,

## PERFUMERY

which is not the case with *Vanilla pompona*. But splitting will impair the commercial value, so care is taken not to allow the beans to hang too long on the vines. On the other hand, if picked too soon, the resulting cured beans will be of poor value.

The vanilla plant is one which only requires a rich top soil, and, given the suitable climate, any soil of volcanic origin or where there is plenty of humus on top is favourable to its growth. Propagation by seed is not commercially possible, and the plants are always propagated by cuttings. The length of the cuttings is very variable—sometimes a foot, sometimes 3 to 4 feet. In planting short cuttings the base is inserted into the ground about 1 inch, and a stick put close to it for it to commence climbing on. At least two joints of the stem must be above the ground. As the plants gradually become exhausted, it is necessary to replace a part of the plantation every year, and some planters reserve annually a certain part of the plantation, where no flowers are fertilised, so as to strengthen them for bearing the following year. Strong healthy plants are thus held in reserve for cuttings for new plants. According to Delteil, the best months for making cuttings are, in Réunion, November, December, January, and February, the periods of heavy rains and great heat. In the Malay Peninsula, where there are seldom dry periods of over a week or so, almost any time is suitable so long as there does not happen to be a dry spell at the time.

The vanilla, being a climbing plant, requires supports to develop normally. In the wild state it climbs on forest trees in the more open parts of a forest by preference, and attains a great height. When cultivated, it is essential to keep its growth reasonably low, as otherwise hand fertilisation and the gathering of the beans become matters of great difficulty. Where there are already suitably branched trees on the ground that can be utilised, or which by pruning and topping can be made suitable, these should be used, supplementing them with posts and trellis where necessary.

If trees have to be planted, numerous varieties are available, but some discrimination is required in their choice, as they should not exhaust the soil of the particular constituents required by the vanilla plants, and they should be strong enough to resist storms. They should, too, be of sufficiently rapid growth to be economically useful. When the fruits are gathered, they have no odour of what is known commercially



as "vanilla." This is produced by the fermentation which goes on during the curing process, of which several different varieties are used.

The so-called curing of the beans is the most important part of the vanilla planter's work, and if carried out unskilfully, the resulting commercial vanilla beans will be a failure. If the beans are allowed to become fully ripe on the plants, they commence to split, and as the ripening proceeds the bean becomes dark in colour and the vanilla odour develops. This is accompanied by the development of essential oil, which exudes, and is known as "balsam of vanilla." In order to hasten the very slow process of ripening and, at the same time, to avoid the splitting of the beans, artificial processes, known as "curing," are resorted to, with the result that the beans keep their condition, which they will not do when allowed to ripen on the vines.

The principal methods of curing vanillas employed to-day are the following —

(1) *The Boiling Water Process* — This process was first used in Réunion in 1851, and has been very successful. At first boiling water was used, but to day it is more customary to use water at a somewhat lower temperature, and keep the beans immersed for a longer period. In Madagascar the curing process is to a great extent in the hands of specialists from Bourbon, and, subject to the modifications as to temperature and time of immersion of the beans, is carried out as follows (Fauchère, *Le Journal d'Agriculture Tropicale*, through *R & E O R.*, 1914, 152). In certain centres, where only small plantations exist, these specialists prepare the crops of several planters, receiving in this case so much per kilogram of vanilla ready for market

This preparation consists of several operations —

(a) *Boiling* — This kills the pods and prevents their dehiscence. Great pots of water are brought to the boil, the baskets of pods are immersed and kept in the water for fifteen or twenty seconds (*vide supra*)

(b) *Exposure to the Sun* — The pods are drained, spread on tables covered with woollen cloths, and left exposed to the sun until about two in the afternoon. Then they are rolled up in the cloths and kept in a warm room until next day. Exposure to the sun lasts from four to ten days, according to the weather. This part of the process must not be unduly prolonged, and when the pod has become supple and of a chocolate tint with metallic reflection, it is time for the next process.

(c) *Drying*.—The pods are taken to the drying room, which has a western exposure, and with windows which are opened in the middle of the day when the sun is hottest. The pods, placed upon openwork shelves arranged round the room, remain there thirty to forty days, until they are dry. During the drying the operator must not relax his vigilance for a moment, and much experience is required to determine the exact degree of dryness required. When sufficiently dry, the pods are hermetically sealed up in tin boxes to prevent further desiccation. Thus the preparation of vanilla takes about two months, during which the pods have lost about three-quarters of their weight. Although the preparation is a very delicate operation, many planters in Madagascar are emancipating themselves from the tutelage, sometimes tyrannical, of the experts, and are treating the vanillas themselves, and not without success. Then the pods are sorted, measured, and packed into uniform lots according to quality and length. Fifty pods of equal length, tied in three places with coarse thread, go to each bundle. The bundles, of equal length, are packed in tins, each containing from 10 to 12 kg. No packing is used that could damage the odour of the vanillas, and finally the tins are soldered down and packed by threes into wooden cases for the European market.

(2) *The Mexican Process*.—This process, according to Ridley (*loc. cit.*), is carried out as follows. As soon as the beans are gathered they are piled up in heaps in a shed, which protects them from the rain and sun, and in a few days, when they begin to shrivel, they are submitted to what is known as the sweating process. The method by which this is carried out depends on the weather conditions. If it is warm and fine, the pods are spread out in the early morning on a woollen blanket and exposed to the rays of the sun. About midday or one o'clock in the afternoon, the blanket is folded over the pods and the bundle left in the sun for the remainder of the day. In the evening the vanilla is enclosed in airtight boxes, so that it may sweat during the whole of the night. The next day the pods are again exposed to the direct action of the sun. They then become dark coffee coloured, the shade being deeper according to the success of the sweating operation. If the weather is cloudy, the vanilla is made into bundles, and a number of these are packed together in a small bale, which is first wrapped in a woollen cloth, then in a coating of banana leaves, and finally the whole is enclosed in a thick matting and sprinkled with water. The bales containing the

## PERFUMERY

largest beans are now placed in an oven heated to 140° F. When the temperature has fallen to 113° F., the smaller beans are introduced and the oven closed tightly. Twenty-four hours afterwards the smaller beans are taken out, and twelve hours later the larger ones. During this process the vanilla has sweated and acquired a fine chestnut colour. The pods are then spread on matting and exposed every day to the sun for nearly two months. When the drying is nearly complete, sun heat is no longer required, and the pods are spread out in a dry place till they are sufficiently dry. They are then tied into bundles for market. This process is sometimes employed in Réunion as well as in Mexico.

(3) *The Guiana Process.*—The beans are packed in dry ashes and left there until they commence to shrivel. They are then taken out, wiped, smeared with olive oil, and tied at the lower end to prevent dehiscence, after which they are left to dry in the open air.

(4) *The Peruvian Process.*—In this process the beans are dipped in boiling water, tied at the lower end, and hung up in the open air. After about three weeks' drying, they are smeared with oil and, after a few days, are tied up in bundles.

Drying by means of calcium chloride is a method which has been described in a report of the British Consul in Réunion in 1897, and published in the *Kew Bulletin*, 1898, 43. It is claimed that there is less loss of odour when the water is absorbed from the beans by means of a hygroscopic substance, such as calcium chloride, than by drying them in the open air.

Consideration may now be given to the special conditions obtaining in regard to vanilla in a few of the more important producing centres.

(1) **Tahiti** is one of the principal producing centres in regard to quantity, the total output sometimes reaching to 40 per cent. of the world's production. Tahiti commenced to produce vanillas about 1850, but the quality of the beans began to deteriorate, and Tahiti beans are less valued than other varieties. They are poor in vanillin and have an odour recalling that of a mixture of vanilla, heliotropin, and plums. It has been suggested by Busse that the cause of this deterioration is due to the fact that the plant has become a local variety altered from the original by climatic conditions. It has also been suggested that the methods of preparation are at fault, and that the habit of the Chinese of buying up the green pods and preparing them in a rough and

## PERFUMERY

ready manner, and then mixing these inferior beans with properly prepared pods, is to some extent responsible for the deterioration. But it is not quite certain that the Tahiti plant is actually the true Mexican *Vanilla planifolia*. At all events, in the season 1909-1910 Tahiti produced 180 tons of vanilla beans out of a world's crop of 390 tons.

(2) Mexico.—A large quantity of vanilla of fine quality is produced in Mexico both from cultivated and uncultivated plants. Plantations are established either in open fields or in virgin forests. In the latter case, all shrubs, climbing plants, and such large trees as would cut off too much light are cut down, leaving only those trees which are required to serve as supports for the vanilla plants. Experienced planters give preference to those trees which produce a milky sap, as the orchid attaches itself to the bark by means of its aerial roots, which are produced at the nodes, and by which the plant nourishes itself. The subterranean roots, which do not penetrate far beneath the surface, are comparatively insignificant. The cuttings, which in Mexico are 3 to 4 feet long, are imbedded as far as three joints, the leaves being first stripped off this part, in a shallow trench, two against each tree, the remainder of the cutting is tied to the tree. These cuttings, which must be carefully cultivated and kept free from adjacent weeds, will bear fruit in the third year. Planting takes place in the rainy season, and if there is not much rain, plenty of watering is necessary. Where a plantation is set out in an open field, low-lying ground is chosen, which is first ploughed up and sown with maize. Whilst this is growing, young trees of the fig type, which produce a considerable amount of latex, are allowed to grow up, and in a year or eighteen months these are strong enough to support the young vanilla vines.

Although it is clear that *Vanilla planifolia* and *Vanilla pompona* are the two cultivated species, there are a number of names applied locally to, possibly, some slight variations in form, or possibly, in some cases, to some different species growing wild, which occasionally provide pods which are harvested, and, although of little odour value, were at one time mixed in with the true vanilla beans. For all practical purposes it may be assumed that, apart from vanillons obtained from *Vanilla pompona*, the remainder of the commercial beans are derived from *Vanilla planifolia* in some variety or other, to which specific rank has at some time or other been incorrectly assigned. According to Sawer ("Odorographia," i, 146), there are five

## P E R F U M E R Y

sorts of vanilla plants known locally in Mexico by the following names :—

(a) *Vanilla coriata*. This is held in greatest esteem for the quality of its pods, which are divided commercially into five classes, the first being long fleshy pods full of pulp and seed, and with a very fine skin; the second, called *Vanilla chichasina*, about half the length of the preceding, and with a thick skin, not so fine in flavour, but still sometimes sold with it, also bearing the same vernacular name, "loc," "leq," or "leg," abbreviated from "legitimate." The third sort is the *Vanilla sacata*, having a finer cuticle than the first. The fourth, *Vanilla resequata*, is small, dry, and only a fourth of the length of the preceding. The fifth quality is called *basura*, and is a very inferior product.

(b) *Vanilla sylvestris* or *simarona*, a wild species (*sed quere?*), with smaller fruit than the *coriata*. This plant appears to be botanically identical with the *coriata*, but as it is found growing in dense woods whose foliage deprives it of sunlight, its pods cannot develop.

(c) *Vanilla mestica* (*mestica* meaning in English middle, medium, or average). This bears a rounder pod than other varieties. The green unripe pods are spotted with brown, and the ripe pods are very apt to split open.

(d) *Vanilla puerca* (la porcine, vanille cochon, swine vanilla). This variety bears much smaller pods than those of *Vanilla coriata*; they are also rounder in form, of a darker green colour when unripe, and exhale an unpleasant odour during the process of curing; hence the name.

(e) *Vanilla pompona*. This plant bears a very thick short fruit covered with a very thin skin. When this fruit begins to dry, it acquires a very fine perfume (recalling that of heliotrope). The perfume is, however, considered less sweet than that of the *coriata*, and it is apt to go off or disperse by evaporation if tied in bundles alone, so it is sometimes packed up with one of the (a) varieties. It is comparatively low-priced, and is commercially designated *vanillon*.

(3) **Madagascar**.—According to Fauchire, (*see P. & E. O. R.*, 1914, 152), the cultivation of vanilla is the most important industry in Madagascar. In 1912, about 100 tons, valued at 4,000,000 francs, were produced. The variety cultivated here is *Vanilla planifolia*. It is indigenous to Mexico, having been first introduced into the Natural History Museum at Bourbon, whence

## P E R F U M E R Y

it was carried to Madagascar forty years ago. Formerly it was cultivated chiefly in the districts of Mahanora and Vatomandry, on the east coast, and in the island of Nosy-Bé. After the French conquest, the culture rapidly spread into the neighbourhood of Maroantsetra and Andevoranto, but the plant seems to have taken most kindly to Antalaha. A few years ago Antalaha was an almost unknown village, to-day this little east coast port exports about 1,500,000 francs' worth of vanilla per annum. Vanilla can grow in various kinds of soil. In Madagascar it flourishes in the granitic alluvial earth peculiar to the valleys of the rivers running eastward, on the sandy plains near the coast, on soils derived from the decomposition of basaltic rocks, and also in volcanic earth. The last two appear to be the most favourable. On the alluvial soil of Mahanora, Vatomandry, and Tamatave are some fine vanilla plantations, but here the plants are delicate and more difficult to cultivate than those upon the volcanic earth of Nosy-Bé or the basaltic soil of Antalaha, and less productive. From analyses of soil made in the laboratory of the Colonisation Service at Tananarive it appears that phosphoric acid is very beneficial to vanilla. In fact, the soils at Nosy-Bé are extremely rich in both phosphoric acid and potash. These soils contain a minimum of 4 per cent phosphoric acid, while that in the crater of a volcano, and known to be very fertile, showed 7.5 per cent. From this it is fair to assume that the judicious use of phosphatic and potash manures would be a great boon to the vanilla. As regards climate, one may justly conclude that this plant requires a humid climate, certainly a long season of dryness is prejudicial, while systematic irrigation has been found highly beneficial. Vanilla plantations should be established among shady trees, such as *Albizia Lebbek* or banana, and if the land selected be covered with trees and shrubs, sufficient of these are left when clearing the land to provide plenty of shade. Other trees, such as the mango, badamier (*Terminalia catappa*), baro (*Hibiscus tiliaceus*), are also used, but in Madagascar the filao, so much employed in Réunion as a support for the vanilla, is not used. The support commonly used is the *Jatropha Curcas*, but the "candle wood," *Dracana tessclata*, is frequently found also. The supports are placed usually 1½ or 2 metre apart in rows, distant about 2 metres from one another.

Vanilla is propagated by cuttings not less than 1½ metres long; these are rather expensive, as much as fifteen to twenty or even twenty-five centimes being paid for good specimens. Great

## PERFUMERY

Attention is needed; vanilla cannot exist where weeds are, and too much exposure and too much shade are equally prejudicial. The stems need to be constantly raised up, trained round the supports, and at times pruned. The principles of pruning are not well known, and each planter has his own ideas. The soil is periodically covered with vegetable matter, which, on decomposition, enriches the land with humus very favourable to the vanillas. Banana stems answer the purpose admirably. The first flowers appear in the third year, and if one uses very long cuttings the first flowering may even appear after two years. In Madagascar flowering begins in June, and lasts until October or November. The pods mature six or seven months after fecundation, and the ripeness is recognised by the yellow tint of the extreme tip.

The culture of vanilla in Madagascar has attained great importance, and a notable increase may be expected in years to come. Though there is every encouragement for the colonists to extend this culture, they should remember the bad years of 1906-7-8, where the price fell so low as to leave no profit to the grower, and provide against any recurrence of this. There is danger in the present practice of growing vanilla only, for every growth has its periodic bad seasons, and if coffee, cocoa, manioc, and coconut were cultivated concurrently with vanilla, disaster might be averted; and, in fact, a decided movement is just being made towards polyculture.

Beyond certain insect enemies, the vanilla has few dangers to contend with. Certain species of bug pierce the tender pods and destroy them, notably the *Memia vicinia*, though there are other varieties of this pest not yet determined. The best method of combating this trouble is fumigation with cyanide, as employed in the United States.

In regard to the yield of pods, on the east coast of Madagascar 600 kg. of green pods per hectare is considered a good crop, but the vanilla is a capricious plant, and may at times give as much as 1,000 kg. per hectare.

There is, however, some difference of opinion as to the suitability of banana trees for shading the vanilla vines. Morsaine condemns it for several reasons. It is insecurely attached to the ground and is said to be uprooted by a very small amount of wind, and falls and crushes the vines. Further, the banana exhausts the soil of so much potash and lime that it is said to injure the nutrition of the vanilla vines. These objections are probably academic, as.

## PERFUMERY

certainly in Malay, banana trees will stand storms which uproot very big trees; and the dead leaves and stems of this tree are dug into the soil as manure, thus restoring the potash and lime salts.

(4) **Réunion.**—Bourbon vanillas are amongst the most highly esteemed of all. Although the plant was introduced into the island in 1793, it was not until much later that the plant was cultivated for commercial purposes. Its cultivation began to increase very considerably about 1870 onwards, and to-day the output from Réunion ranks second only to that of Mexico. The methods of cultivation and curing are much the same as in Madagascar; indeed, as has been mentioned, the methods in use there have, in the main, been borrowed from Réunion. The principal trees used for shade in Réunion are the blackwood (*Acacia Lebecki*), the dragon tree (*Dracena Draco*), the jack tree (*Astocarpus integrifolia*), the ouatier (*Bombax Matibasicum*), and the pignon d'Inde (*Jatropha Curcas*). According to de Floris (*Journal of the Agricultural Society of India*, vol. xi., pt. iv.), the protecting trees should be planted 6 feet apart in east and west rows. They should be pruned from time to time so as to produce a half shade, so that only half a day's full light reaches the vanillas directly they are planted against the supports. A ground sloping to the west is preferable, as it gives the plants more warmth and less wind.

Apart from the above, vanilla is cultivated and exported on a commercial scale in Seychelles, the Comoro Islands, Guadeloupe, and Martinique, and on a small scale in Mauritius, Java, and Zanzibar.

The odoriferous constituents of vanilla beans do not exist, or at most only to a very small extent, in the bean until a process of fermentation has taken place in the curing stage. According to Lecomte, a ferment having the characters of an oxydase is present in most parts of the vanilla plant. In the ripe fruit it is localised in the parenchyma of the pericarp. The cells containing raphides are free, apparently, from this oxydase, which is principally found in the cells surrounding the fibrovascular bundles. Lecomte states also that in the sap of the plant there is a second ferment, which is able to hydrolyse starch, and which, when allowed to react upon the glucoside coniferin, produces substances giving the same reactions as those regularly yielded by the bodies to be found in the tissues of the vanilla bean. Lecomte considers that the glucoside coniferin is present in the bean, and is transformed by



## P E R F U M E R Y

the hydrolysing ferment into coniferyl alcohol and glucose, and that the coniferyl alcohol is then transformed into vanillin by the action of the oxydase. The following analyses of two samples of vanilla beans are due to König, but they do not give the vanillin content :—

|   | 1.              | 2.              |
|---|-----------------|-----------------|
| Water . . . . .                           | 25.85 per cent. | 30.94 per cent. |
| Nitrogenous matter . . . . .              | 4.87            | 2.56            |
| Wax and fat . . . . .                     | 6.74            | 4.68            |
| Sugars (reducing) . . . . .               | 7.07            | 9.12            |
| Non-nitrogenous ex-<br>tractive . . . . . | 30.5            | 32.9            |
| Cellulose . . . . .                       | 19.6            | 15.27           |
| Ash . . . . .                             | 4.73            | 4.53            |

Vanillin may be determined in the beans by the following process, due in the main to Tiemann and Haarman (*Berichte*, viii., 1115). From 30 to 50 grams of the beans are minced and well shaken during six to eight hours with about 1,000 c.c. of ether. The clear liquid is filtered and the vanillas again exhausted with a fresh quantity of about 1,000 c.c. of ether, and the maceration, with constant shaking for another two hours, and the extraction repeated a third time with 500 c.c. of ether. The residue on the filter is washed with a small quantity of ether, when the exhaustion may be considered complete. The united ethereal extracts are now concentrated by distilling off the bulk of the ether to about 150 to 200 c.c. The liquid is then transferred, with the usual precautions, to a separator, and is three times (twice only is recommended in the original paper) extracted with a half-saturated solution of sodium bisulphite. The sodium bisulphite solutions are mixed and well washed with ether in order to remove uncombined impurities. It is then decomposed with dilute sulphuric acid, and the sulphurous acid driven off by gentle heat. The vanillin is liberated and is extracted three times with ether, the ether driven off at a low temperature, and the vanillin dried in a desiccator for a short time and weighed. The following results were obtained by Tiemann and Haarman for beans of various origins :—

### *Maacan*

|                             | Per cent. |
|-----------------------------|-----------|
| 1. First quality . . . . .  | 1.69      |
| 2. " " " . . . . .          | 1.86      |
| 3. Medium quality . . . . . | 1.32      |

## PERFUMERY

### *Bourbon*

|                               |      |
|-------------------------------|------|
| 1. First quality . . . . .    | 2.48 |
| 2. " " . . . . .              | 1.91 |
| 3. " " . . . . .              | 2.90 |
| 4. " " . . . . .              | 1.97 |
| 5. " " . . . . .              | 2.43 |
| 6. Medium quality . . . . .   | 1.19 |
| 7. Inferior quality . . . . . | 1.55 |
| 8. " " . . . . .              | 0.75 |

### *Java*

|                             |      |
|-----------------------------|------|
| 1. First quality . . . . .  | 2.75 |
| 2. Medium quality . . . . . | 1.56 |

Where vanillas have been adulterated with such substances as benzoic acid (which has been done at times by adding an alcoholic solution of benzoic acid to the beans in order to imitate the "frosted" or crystalline appearance of the better-grade vanillas, on which vanillin has crystallised out), these adulterants will be found in the ethereal extract after removing the vanillin as above described, as neither benzoic acid nor any of the probable other adulterants are absorbed by sodium bisulphite solution.

Hanus (*Pharm. Zeit*, 50, 1022, 157) has recommended the following method for the determination of vanillin in the beans and preparations thereof. Three grams of the crushed beans are exhausted with ether in a Soxhlet tube, the ether distilled off at a low temperature, the residue dissolved in a little ether, the solution filtered, and the filtrate cautiously evaporated. The residue is treated with 50 c.c. of water at 60° on a water bath; 0.25 gram of *meta*-nitrobenzhydrazide is then added to the aqueous solution in a stoppered flask, which is kept for two to three hours at 60° and then set aside, with occasional shaking, for twenty-four hours. The vanillin is precipitated quantitatively as vanillin-*meta*-nitrobenzhydrazone  $\text{NO}_2\text{C}_6\text{H}_4\text{NH}_4\text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_3(\text{OCH}_3)\text{OH}$ . The precipitate is washed with three successive quantities of petroleum ether to remove fat, then washed with water, and then again with petroleum ether, and then dried at 100° for two hours. The weight multiplied by 0.4829 gives the amount of vanillin present.

Walbaum (*Schimmel's Report*, October, 1909, 142) made an ethereal extract of Tahiti vanillas and, after removing the vanillin by means of sodium hydroxide solution, steam distilled the residue. He obtained 7 grams of a light brown oil having a

fragrant odour, in which he detected anisic aldehyde and anisic alcohol.

Where a perfumer has made his own spiritous essence of vanilla, no analysis is, as a rule, required; but where he buys a ready-made essence an examination is sometimes necessary.

In the examination of vanilla essence, the determination of the so-called lead number has been advocated by American chemists. As this figure depends on the amount of organic matter present that will precipitate lead from a solution of lead acetate, and as there is a practically inexhaustible number of simple organic substances that will precipitate lead under these conditions, it is obvious that the determination is of very little value. If it be necessary to determine whether a given liquid is, in fact, an extract of vanilla beans or merely a solution of vanillin, the "lead number" will be of value. But, as the slightest addition of organic matter entirely vitiates the results obtained, the process cannot be regarded as having any scientific value. It merely enables the analyst to discriminate between those essences of vanilla which have been produced from vanilla beans and those which have not, on the assumption that the manufacturer has produced them in a certain way, which in the case of the dishonest manufacturer is most improbable.

Winton and Silvermann (*Jour. Amer. Chem. Soc.*, 24, 1128) have recommended the following method for examining essence of vanilla. Twenty-five grams of the essence are evaporated on a water bath at 80°, to remove the alcohol, water being added from time to time to retain the original volume. After removal of the alcohol, a normal solution of acetate of lead is added, drop by drop, until no further precipitate is formed. The liquid is then filtered through a moistened filter, and the precipitate is washed three times with a few cubic centimetres of hot water. The filtrate is cooled, and is then extracted with ether by repeated shaking in a separator. The combined ether extracts are transferred to another separator, and are extracted four times with 2 per cent. ammonia. The ammonia solutions are combined and slightly acidified with dilute hydrochloric acid. The resulting liquid is then extracted with ether several times, and the ether evaporated at room temperature, dried over sulphuric acid, and weighed. The residue may be taken as vanillin; but it should be warmed with petroleum ether, which is decanted, several times, and if any undissolved residue is left, it is deducted from the residue weighed as vanillin. If coumarin be present, it will be found in the

ethereal solution from which the vanillin has been extracted by ammonia.

Winton and Bailey (*Jour. Amer. Chem. Soc.*, 1899, 256) prefer to determine vanillin, coumarin, and acetanilide, which is sometimes present as an adulterant of artificial vanillin, in the following manner: Twenty-five grams of the essence are weighed into a 200 c.c. beaker, marked at 25 and at 50 c.c. The essence is diluted with water to 50 c.c. and evaporated on a water bath to 25 c.c., at a temperature not exceeding 70°. It is again made up to 50 c.c. with water, and evaporated to 25 c.c. Solution of lead acetate is then added, drop by drop, until no further precipitation takes place. The liquid is then, after being well stirred, filtered through a moistened filter paper and washed three times with hot water, so that the total filtrate and washings do not exceed 50 c.c. The filtrate, when cold, is shaken with 20 c.c. of ether in a separator. The ether is separated and the liquid extracted with three further portions, each of 15 c.c., of ether. The combined ether extracts are then shaken with 10 c.c. of 2 per cent. solution of ammonia, and with three subsequent portions of 5 c.c. each. The ethereal solution is reserved (B), and the combined ammoniacal solutions are rendered slightly acid with dilute hydrochloric acid. The liquid is then extracted four times with ether, and the ether evaporated, the residue dried at room temperature, and then in a desiccator, and weighed (A). If acetanilide be absent, this may be taken as pure vanillin, which should melt at about 80°. If acetanilide has been detected, the residue should be dissolved in 15 c.c. of 10 per cent ammonia and the liquid twice shaken with ether. The ether, on evaporation, will leave a residue of acetanilide, which is dried at room temperature, and then in a desiccator, and the weight deducted from that of the "vanillin" (A) previously weighed. The total amount of acetanilide is the amount thus obtained, together with that present in the ethereal solution (B) reserved as above described. The latter is transferred to a tared dish and the ether allowed to evaporate at room temperature. The residue is dried in a desiccator and weighed. It is then extracted several times by stirring well with petroleum ether, which is decanted each time. If the residue is thus completely dissolved, it may be taken to be entirely coumarin. Any undissolved residue is probably acetanilide (melting at 112° to 113°), and its weight deducted from the total residue gives the coumarin. The acetanilide here found is added to the amount extracted with the vanillin.

• Dox and Plaisance (*Amer. Jour. Chem. Soc.*, 1916, 481) give the following method for the determination of vanillin in essence of vanilla. It depends on the use of thiobarbituric acid in the presence of 12 per cent. hydrochloric acid as a precipitant. The precipitate consists of the condensation product methoxy-hydroxy-benzal-malonyl-thiourea. The method of procedure is as follows: 25 c.c. of the essence are freed from alcohol by evaporation, transferred to a 50 c.c. flask, and filled to the mark with a solution of lead acetate. After standing for several hours at about 37°, the contents of the flask are filtered through a dry filter. The filtrate should be of a pale straw colour, indicating the absence of caramel. Forty cubic centimetres of the filtrate are transferred to another 50 c.c. flask, and sufficient concentrated hydrochloric acid is added to the flask up to the 50 c.c. mark. After standing for a short time, the lead chloride is filtered off and 40 c.c. of the solution taken for determination. On adding thiobarbituric acid in 12 per cent. hydrochloric acid solution, an orange-coloured precipitate results, which, after standing overnight, is filtered on a Gooch filter, washed with 12 per cent. hydrochloric acid, and dried at 98°. A correction is made for the solubility of the condensation product, which amounts to 2.6 mg. The conversion factor for the vanillin equivalent of the weight of the condensation product is 0.5162, after making the corrections for solubility and the aliquot portion of the liquid used.

The estimation of vanillin, either alone or when in admixture with heliotropin or coumarin, has been the subject of numerous other researches, and the following methods may be described:—

Von Fellenberg (*Schimmel's Report*, 1916, 93) describes a colorimetric process depending on the colour resulting when vanillin reacts with isobutyl alcohol and sulphuric acid. As the vanillin is unevenly distributed in the bean, the best sample is taken by using pieces equally far apart from the centre, together with a centre portion. About 1 gram is used for the determination. This sample is cut in transverse sections of 1 to 2 mm. thickness, but which ought still to hang together in one spot, placed in a small flask, and extracted four times under a reflux condenser with altogether 90 c.c. of water, by boiling each time for three to five minutes and pouring the slightly cooled extract into a measuring flask of 100 c.c. After the second extraction, the vanilla is squeezed over the funnel, and finally kneaded several times with a few cubic centimetres of water. The brown extract is brought up to 100 c.c., vigorously shaken with 0.5 gram of Fuller's

earth, and then filtered. Fifty cubic centimetres of the filtrate are shaken five times with ether free from alcohol, 50 c.c. of ether being used the first time, and 25 c.c. for each treatment afterwards. The ethereal solution is dried over calcium chloride for from five to ten minutes, filtered, the filter washed with ether, the latter then being removed by distillation and, at last, by blowing air through. The residue is heated with 30 c.c. of water to 50° or 60°, in order to separate the vanillin from the small particles of wax, and made up to 100 c.c. and filtered. To 5 c.c. of the filtrate, in a measuring flask, 5 c.c. of a 1 per cent. solution of isobutyl alcohol in 95 per cent. ethyl alcohol are added, and afterwards 20 c.c. of concentrated sulphuric acid are allowed to flow in, the flask being held slightly inclined. It is then shaken and allowed to stand for forty-five minutes. In a similar way  $\alpha$  type solution is treated, which has been obtained by dissolving 0.1 gram of pure recrystallised vanillin, previously dried until the weight remained constant. The colorations resulting are compared in a colorimeter, it being admissible to dilute the solutions with dilute sulphuric acid (1 volume of concentrated sulphuric acid and 1 volume of water). The vanilla content amounts to  $\frac{4a}{g}$ ,  $a$  corresponding to the number of milligrams of vanillin found in the final solution, and  $g$  to the weight in grams of the vanilla used. The value  $a$  is obtained with the aid of tables accompanying the treatise.

An elaborate examination of the methods for the determination of vanillin, piperonal (heliotropin), and coumarin has recently been published by Radcliffe and Sharples (*P. & E. O. R.*, November, 1924, 396; December, 1924, 437; January, 1925, 20), which at the time of this work going to press is still unfinished, so that the concluding portions will be found in the succeeding issues of the publication quoted.

The principal methods dealt with are those of Hanus, Feinberg, Dox and Plaisance, Doherty, and certain volumetric methods useful where nothing is present to interfere with the use of ordinary indicators.

Hanus proposed to use *para*-bromophenylhydrazine or  $\beta$ -naphthyl-hydrazine as precipitants of Vanillin (*Zeit. Nähr. Untersuch. Genussm.*, 1900, 531), but abandoned these, as foreign bodies, especially fats, interfered with the results. He prefers the use of *meta*-nitrobenzoyl-hydrazide (*ibid.*, 1905, 587). The details of this process have been described above.

Feinberg (Eighth International Congress of Applied Chemistry, Section 1) prefers to use *para*-nitrophenyl-hydrazine as a precipitant. His process is as follows :—

“Twenty-five cubic centimetres of a 0.75 to 1 per cent. aqueous solution of vanillin diluted with 75 c.c. of water at 60° are treated with 25 c.c. of 2N hydrochloric acid containing 0.6 gram of *p*-nitrophenylhydrazine added drop by drop from a pipette. The mixture is stirred vigorously while the precipitant is added, and the precipitate allowed to stand for thirty minutes before filtration. It is washed on the Gooch crucible with a little dilute hydrochloric acid, and finally with water until free from acid.”

The first experiments using this method gave very low results, which were found to be due to the use of excess of hydrochloric acid. Using for the washing solution 25 c.c. of N/5 acid, the following results were obtained :—

| Weight vanillin take    | Weight found  | Per cent. |
|-------------------------|---------------|-----------|
| 0.2500 gram             | 0.2510 gram   | 100.4     |
| 0.2500 „                | 0.2513 „      | 100.5     |
| 0.2500 „                | 0.2500 „      | 100.0     |
| 0.2500 „                | 0.2508 „      | 100.3     |
| 0.2500 „                | 0.2490 „      | 99.6      |
| Weight piperonal taken. | Weight found. | Per cent. |
| 0.0500 gram             | 0.0510 gram   | 102.0     |
| 0.0500 „                | 0.0508 „      | 101.6     |
| 0.0500 „                | 0.0500 „      | 100.0     |
| 0.0250 „                | 0.0247 „      | 98.8      |

*para* Nitrophenylhydrazine has no action on coumarin. The *p*-nitrophenylhydrazones of vanillin and piperonal are easily soluble in alcohol, and thus alcoholic solutions of aldehydes cannot be employed. Piperonal *p*-nitrophenylhydrazone crystallises from alcohol in red crystals having a fine steel blue lustre.

Doherty (*Jour and Proc. Roy. Soc. N.S.W.*, 1912) considers the following process for essence of vanilla to be the most reliable :—

“Fifty cubic centimetres are distilled, the distillate being utilised in the determination of the alcoholic strength, and in the determination of volatilised vanillin, which it invariably contains. The residue is acidified and extracted in a continuous extraction apparatus, or extracted in the ordinary way, four times with ether. The ether, which contains the whole of the vanillin less the small amount which came over in the alcoholic distillate, is removed by

## PERFUMERY

evaporation or distillation from the residual vanillin, etc., until only about 3 c.c. remain. This is treated with 20 c.c. of a 10 per cent. aqueous solution of sodium bisulphite and, after shaking and contact for at least an hour at ordinary temperature, is well washed with ether. This ether is treated with a further 5 c.c. of the bisulphite solution, and, after separation, may be washed and evaporated and the residue examined for the presence of foreign substances, such as coumarin, benzoic acid, acetanilide, etc. The bisulphite solution is added to the main portion, which is then acidified with dilute sulphuric acid, and this must be added in sufficient quantity to decompose the bisulphite, and so set free the aldehyde. At least 2.5 grams of  $\text{H}_2\text{SO}_4$  must be added. The sulphurous acid produced in the reaction may be eliminated from solution by passing carbon dioxide through it. The vanillin is then extracted with chloroform, using 20 c.c., 15 c.c., and 10 c.c. respectively. The chloroform solutions are combined and washed twice with distilled water, to free them from acid, and allowed to spontaneously evaporate. The wash waters are added to the chloroform-extracted liquor, and this is separately extracted with ether, which is evaporated, and whatever residue of vanillin there may be left is added to the alcoholic distillate at first obtained. The residue from the chloroform, which contains practically the whole of the vanillin, after drying in a vacuum over calcium chloride, is weighed in a tared dish. If properly carried out, the resultant vanillin is generally pure enough, though at times it may contain some impurity, and may even contain some foreign aldehydic body, such as piperonal. The melting point should be taken, and a known portion dissolved in alcohol and compared colorimetrically with a standard solution of pure vanillin, using the reaction occasioned by bromine water and ferrous sulphate. This colorimetric method is used in determining the amount of vanillin in the alcoholic distillate.

"One cubic centimetre of the sample is treated in a small separator with 10 c.c., and then with 5 c.c., of ether, which, on separation, is allowed to evaporate in a warm place on about 30 c.c. of distilled water. When all the ether has evaporated, the watery solution is filtered through a moistened filter to the 50 c.c. mark in a Nessler glass. Ten drops of a freshly prepared saturated solution of bromine water and 10 drops of a 10 per cent. solution of ferrous sulphate are added in the order mentioned. The colour is compared with a 0.2 per cent. solution of pure vanillin (tested by titration with decinormal alcoholic potash), either by simple



## P E R F U M E R Y

Nesslerising or, preferably, with a Dubosc colorimeter. It may further be simplified by adding the bromine and iron solution to the diluted essence, using 1 c.c. to 50 c.c. of water, comparing with a similar essence whose vanillin content is known."

Experiments were carried out using pure vanillin, which was dissolved in ether and extracted with bisulphite as above. The process is rather long and tedious, but gives consistent results, although 4 to 5 per cent. too low.

| Weight vanillin taken. | Weight found.     | Per cent. |
|------------------------|-------------------|-----------|
| 0.1000 gram . . .      | 0.0991 gram . . . | 99.1      |
| 0.1000 " . . .         | 0.0956 " . . .    | 95.6      |
| 0.1000 " . . .         | 0.0960 " . . .    | 96.0      |
| 0.2000 " . . .         | 0.1902 " . . .    | 95.1      |
| 0.2000 " . . .         | 0.1908 " . . .    | 95.4      |

Piperonal gave the following results :—

| Weight piperonal taken | Weight found.     | Per cent. |
|------------------------|-------------------|-----------|
| 0.1000 gram . . .      | 0.0972 gram . . . | 97.2      |
| 0.1000 " . . .         | 0.0978 " . . .    | 97.8      |
| 0.2000 " . . .         | 0.1920 " . . .    | 96.0      |

Vanillin in presence of coumarin :—

| Weight vanillin taken | Weight found   | Weight coumarin taken. | Weight found.  |
|-----------------------|----------------|------------------------|----------------|
| 0.1000 gram . . .     | 0.0961 gram.   | 0.1000 gram . . .      | 0.0987 gram    |
| 0.1000 " . . .        | 0.0965 " . . . | 0.1000 " . . .         | 0.0990 " . . . |
| 0.1000 " . . .        | 0.0972 " . . . | 0.1000 " . . .         | 0.1040 " . . . |

Vanilla extract :—

Six determinations of vanillin in the vanilla extract gave an average result of 0.2035 per cent. According to the above results, this was taken to be 95 per cent, giving 100 per cent. as 0.2142 per cent. The alcoholic distillate by the bromine method gave 0.0053 per cent. The total percentage,  $0.0053 + 0.2142 = 0.2195$  per cent., was taken as the standard for the extract for comparison with the other methods.

For further details of other processes, the papers of Radcliffe and Sharples above quoted should be consulted.

**VANILLIN.**—This body is methoxy-protocatechuic aldehyde,  $C_8H_8O_3$ , of the constitutional formula  $OH.OCH_3.C_6H_3.CHO$ . It forms fine white needle crystals, melting point  $81^\circ$  to  $82^\circ$ , or when chemically pure,  $82^\circ$  to  $84^\circ$ ; boiling point  $285^\circ$  or, at 15 mm. pressure,  $170^\circ$ . It is the chief odorous constituent of the vanilla pod, which contains about 2 per cent., and also occurs in small quantities in the flowers of *Nigritella suaveolens*, in clove oil,

## P E R F U M E R Y

the oil of *Spiræa ulmaria*, Peru balsam, tolu balsam, Sumatra benzoin (about 1 per cent.), and Siam benzoin (0.15 per cent.). Its presence has also been recorded in asafoetida, beetroot, asparagus, and the seeds of *Lupinus albus* and of *Rosa canina*. It was first prepared artificially by Tiemann in 1874, by oxidation with chromic acid of the glucoside coniferin, which occurs in various coniferous woods found in northern Germany, and melts at 185°. This process was patented by Haarmann and Reimer in 1874 and vanillin was manufactured by it commercially, though on a small scale at Holzminden in Germany. Coniferin was either first hydrolysed by emulsin or by boiling with dilute acid, with formation of glucose and coniferyl alcohol, and the latter oxidised to vanillin, or the glucoside was first oxidised to gluco-vanillin, a crystalline body melting at 170° which on hydrolysis gives glucose and vanillin. In the following year, 1875, Tiemann discovered a much superior method for the production of artificial vanillin by the oxidation of eugenol, the chief constituent of clove and cinnamon leaf oils. This process patented by Tiemann in England in 1876 and almost simultaneously in France by De Lamoignon, is the basis of most of the present-day methods of vanillin manufacture. The eugenol was first separated from clove oil by extraction with caustic soda lye, acetylated by boiling two to three hours with its own weight of acetic anhydride dissolved in acetic acid, and oxidised with potassium permanganate to acet-vanillin. The solution was then made alkaline with sodium carbonate, manganese hydrate filtered off, and the filtrate evaporated, after acidifying with sulphuric acid, the vanillin was extracted with ether and the ether evaporated off. Owing to the formation of a considerable quantity of homovanillin, when eugenol was oxidised, due to the position of the double bond, it was later found preferable to first convert the eugenol into isoeugenol (*gv*) by treatment with potassium hydroxide solution and between 1890 and 1894 several patents were taken out in France and Germany for this conversion under varying conditions, but all depending principally on the action of caustic potash at a high temperature, one of the most important, by Haarmann and Reimer, involving heating the eugenol with a saturated solution of potassium hydroxide in amyl alcohol to 140° for about twenty-four hours. The amyl alcohol is steam-distilled off, the isoeugenol liberated by addition of dilute sulphuric acid, and recovered by distillation in a current of steam. The object of first converting the eugenol into its acetyl-derivative

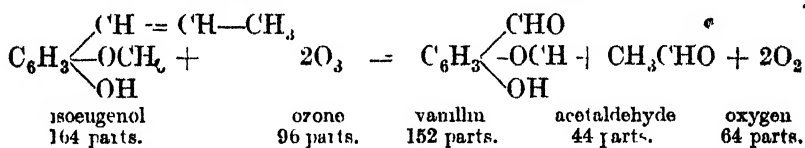
was to protect the hydroxyl group from oxidation, and during the next twenty years a number of other methods of accomplishing this were patented, including formation of compounds with aromatic alcohols, such as benzyl eugenol, by treatment with benzyl chloride, of the eugenol chloride by the action of sulphur chloride or of phosphorus oxychloride, of dinitro-phenyl-eugenol by treatment with dinitrochlorbenzene in presence of an alkali, of methylene dieugenol, and of isoeugenol acetic acid by treatment with chloracetic acid. The special advantage claimed for first converting the eugenol into benzyl-eugenol is that, on subsequent treatment of the benzyl-vanillin (the product resulting from the oxidation) with concentrated hydrochloric acid, benzyl chloride is regenerated and can be again utilised.

In addition to potassium permanganate, many other oxidising agents have been proposed for the conversion of eugenol or isoeugenol into vanillin, including acid sodium or potassium bichromate, chromyl chloride, ozonised air or oxygen, oxygen ionised by ultra violet light (*i.e.*, ozone), hydrogen peroxide, peroxides of soda, barium, lead, or manganese ammoniacal copper oxide or lead or mercury oxide in alkaline solution, or the passage of a mixture of vapour of isoeugenol and air over a platinum spiral heated to dull redness. Other patents have claimed the electrolytic oxidation of a solution of sodium or potassium eugenate, but none of these, with the exception of bichromate or ozone, has assumed any considerable commercial importance. Meisner in 1880 (French Patent 137323) proposed successive oxidation of acetylene, first with potassium permanganate at 35 °C, and after extraction of the acetylene thus formed, with ether, with three separate quantities of potassium bichromate, and in 1907 Fritzsche & Co (English Patent 27927) showed that when potassium bichromate is used the yield can be greatly increased by addition of 20 to 30 per cent of sulphanilic acid or other similar amino-sulphonic acid which prevents formation of resinous substances, while more recently Servers and Giraudan (Swiss Patent 890) claim a similar result for addition of a smaller quantity of an amino carboxylic acid or ester thereof.

Ozone was first proposed for the purpose by Otto and Verley (French Patent 256588, 1895), who recommended bubbling ozonised oxygen through the isoeugenol itself or its solution in acetic acid, and claimed a yield of 50 per cent, an advantage of the process being that it was unnecessary to protect the —OH

## P E R F U M E R Y

group by forming the acet- or other derivative of the isoeugenol, as ozone exerts a selective action, oxidising only the lateral chain. Ten years later the process was considerably improved by Spurge (English Patent 21814, 1905), who ozonised isoeugenol in presence of a strong aqueous solution of sodium hydrogen sulphite, which combines with the vanillin as fast as it is formed, and so prevents its further oxidation to resinous bodies. Ozonised air was employed instead of ozonised oxygen, though the maximum concentration of ozone obtainable in this way was considerably less. With ozonised oxygen a concentration of 2.5 per cent. is readily obtainable, but with ozonised air the maximum concentration attainable on a commercial scale is 2,000 parts per million by volume, or 4 grams per cubic metre. In the actual production of vanillin, however, concentration of ozone appears to play little part, it being quite possible to obtain it with as little as 200 parts per million, and the only objection to the use of such a low concentration, which is, of course, much cheaper to produce, is the volatilisation of so much isoeugenol by the passage through it of such a large volume of ozonised air as is then required. Wood (*Chem. and Met. Eng.*, 1923, 806-808) obviates this difficulty by passing the escaping gases through scrubbing towers containing sodium carbonate and sodium hydroxide, which absorb the isoeugenol. According to Otto and Verley's original patent, 1 kg. of ozone is passed through 1 kg. of eugenol or isoeugenol dissolved in 5 kg. of acetic acid, but this proportion of ozone is much in excess of that required theoretically by the equation—



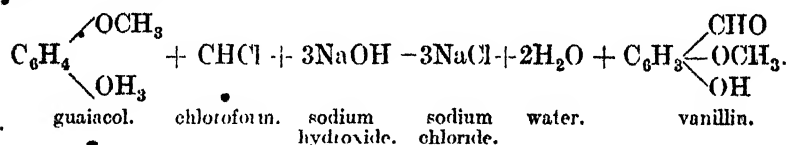
and in the article by Wood quoted above the power required for oxidation by ozone is given as  $\frac{1}{3}$  kilowatt-hour per ounce of vanillin, which at a concentration of 1,000 parts per million would represent only about 15 to 20 grams of ozone per ounce, so that Otto and Verley's estimate of the ozone required would appear to be rather too high.

All processes for the oxidation of isoeugenol to vanillin are claimed by Esclafit (French Patent 421784, 1909) to give a very much increased yield if the isoeugenol is dissolved in a fairly high-boiling hydrocarbon, such as toluol.

In spite of all the precautions that one may take, it is impossible

To avoid the formation of vanilloyl-carbonic acid in appreciable quantity, and several methods have been patented for the recovery of vanillin therefrom, but Guyot and Guy have shown (*Comptes Rendus*, 1909, 149, 928-931) that, when this substance is heated to 170° with an equal weight of dimethyl-*p*-toluidine, vanillin is produced, and may be extracted with ether from the acidified mixture.

As distinct from the processes already mentioned which produce vanillin artificially from naturally occurring bodies, viz., coniferin and eugenol, and are not, therefore, strictly speaking, synthetic, methods have been devised by which artificial vanillin may be produced entirely without the aid of any natural product. As early as 1875, Tiemann showed that methylation of protocatechuic acid by means of methyl iodide formed dimethyl protocatechuic acid, which on prolonged digestion with hydrochloric acid reproduced protocatechuic acid and, at the same time, small quantities of vanillic acid; the latter, on warming with calcium formate, gave vanillin. A year later Tiemann and Reimer discovered a general reaction between phenols and chloroform in alkaline solution, with production of aldehyde-phenols. Thus phenol gives salicylaldehyde, and guaiacol gives vanillin, in accordance with the equation—

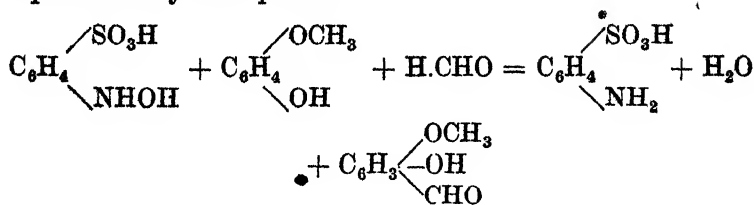


Research in these directions has since gone on side by side with that into the production of vanillin from eugenol, and since 1881 a large number of processes have been patented for the true synthesis of vanillin, most of which fall into two categories: (1) those in which an aldehyde group is introduced into the guaiacol molecule, and (2) those in which the appropriate —OH group in protocatechuic aldehyde is methylated.

Guaiacol is the source of much of the synthetic vanillin manufactured to-day, and though it is a natural constituent of beechwood creosote, and may be obtained therefrom, the synthetic guaiacol prepared by diazotisation of ortho-anisidine is usually employed for the purpose. One of the most important patents is that of Geigy (English Patent 27236, 1898), who condenses guaiacol with formaldehyde in presence of phenyl-hydroxylamine sulphonic acid, produced *in situ* by reduction of nitrobenzene-

## P E R F U M E R Y

sulphonic acid with cast-iron turnings. The reaction may be represented by the equation—



Weiss (English Patent 139153, 1920) heats a mixture of equimolecular proportions of guaiacol and formaldehyde on a water-bath for several hours with *p*-nitro-*o*-dimethylaniline or other aromatic nitroso compound. A few patents (*e g*, Bayer, German Patent 99568, 1897; Roesler, French Patent 189037, 1906) claim production of vanillin by treatment of guaiacol with anhydrous hydrocyanic acid and hydrochloric acid in presence of aluminium chloride, the aldime formed, on hydrolysis with dilute hydrochloric acid, giving vanillin; but these processes have not attained any commercial importance. According to Guyot and Guy (*loc. cit*), a 70 to 80 per cent yield of vanillin may be obtained by condensing guaiacol with  $\alpha$ - $\beta$  diketonic esters, *e g*,  $\alpha$   $\beta$ -diketobutyric ester, and oxidising the product by boiling with copper acetate, which produces copper vanilloyl carbonate, and from this vanillin may be obtained by heating with dimethyl-*p*-toluidine (*vide supra*). A very great disadvantage of this process has been the difficulty in producing the diketonic esters. To obviate this, the Actien Gesellschaft fur Anilin-Fabrikation have recently patented (English Patent 21967) the oxidation, by Guyot and Guy's method, of guaiacyltrichlormethyl-carbinol (easily obtainable by condensing chloral hydrate with guaiacol), after first saponifying it by boiling with water for several hours.

The complete specification (219,676) of a proposed British patent by the Actien-Gesellschaft fur Anilin-Fabrikation, entitled "Improved Manufacture of Vanillin," is as follows—

Guyot and Guy have shown that the condensation products from a diketocarboxylic acid ester and guaiacol can be converted into vanillin by a comparatively simple procedure.

These syntheses of vanillin have hitherto been without technical importance, because of the difficulty that exists in making the acid esters.

According to the present invention, the easily accessible condensation product of chloral hydrate with guaiacol (*Berichte*,

Vol. 56, p. 982) can be used for the same changes as those which the above-mentioned condensation products of diketocarboxylic acid esters undergo. By saponifying the guaiacyltrichloromethyl-carbinol there are obtained directly acids which, by suitable oxidation in the same liquid, become converted into vanillin.

The following examples illustrate the invention :—

(1) Fifty grams of guaiacyltrichloromethyl-carbinol are introduced into 4 litres of water, and the mixture is boiled for twelve hours in a reflux apparatus. After addition of 75 grams of cupric acetate, the solution is further boiled for twelve hours. It is then evaporated to 2 litres and shaken out with ether. The ethereal solution contains 18 grams of vanillin.

(2) Fifty grams of guaiacyltrichloromethyl-carbinol are introduced into 4 litres of water, and the mixture is boiled for twelve hours in a reflux apparatus. After addition of 20 grams of cupric acetate, air is blown in, while boiling is continued for about twelve hours. The vanillin is extracted from the cooled solution, either by ether or chloroform.

(3) Fifty grams of guaiacyltrichloromethyl-carbinol and 20 grams of cupric acetate are introduced into 4 litres of water, and the mixture is boiled in a reflux apparatus for twelve hours, while air is blown through the liquid. The vanillin is obtained from the cooled solution in the manner described above.

(4) Twenty grams of guaiacyltrichloromethyl-carbinol are introduced into 1 litre of water, and the mixture boiled for twelve hours in a reflux apparatus. Thirty grams of cupric acetate are then added, and the boiling continued for one hour. The mixture is then heated in a closed vessel for half an hour at 150°. Vanillin is extracted from the solution thus obtained. The yield is 10.5 grams of vanillin, which amounts to 93 per cent. of that theoretically possible.

(5) Twenty grams of guaiacyltrichloromethyl-carbinol, 30 grams of cupric acetate, and 1 litre of water are heated together in a closed vessel for two hours at 150°. The vanillin thus obtained is extracted.

In their declaration the inventors claim "the manufacture of vanillin by saponifying and oxidising guaiacyltrichloromethyl-carbinol."

Vanillin is very extensively used both in perfumery and toilet soaps, partly as a fixative, and partly for its own odour value. As a flavouring it is also consumed in very large quantities by manufacturers of chocolate, biscuits, confectionery, syrups, and

## PERFUMERY

liqueurs. It is soluble in water, 1 in 90 to 100 parts at 14° and 1 in 20 at 75° to 80°; in 90 per cent. ethyl alcohol (rectified spirit), 1 in 2·5; in isopropyl alcohol, 1 in 1·25; and fairly readily in ether, chloroform, and benzene. It has the character of an acid, due to the presence of the phenolic group, and also of an aldehyde, and methods for its estimation have been based on both these properties, as also on the determination of the methoxyl group, though the latter is too tedious for commercial purposes. Titration of the —OH group with standard alkali to phenolphthalein as indicator is fairly satisfactory, but the end-point is not sufficiently definite when extreme accuracy is required. Numerous gravimetric methods for estimation of vanillin have been proposed, including precipitation and weighing of (1) its  $\beta$ -naphthylhydrazone, factor 0·5208 (Hanus, *Zeit. Untersuch. Nahr. Genussm.*, 1900, 531–537); (2) vanillin *m*-nitro benzoyl hydrazone, by addition of *m*-nitro benzoyl hydrazide, factor 0·4829 (Hanus, *Zeit. Untersuch. Nahr. Genussm.*, 1905, 585–591); (3) its *p*-nitro-phenylhydrazone (Feinberg, *Amer. Chem. Jour.*, 1913, 87); and (4) the semicarbazone, by precipitating with semicarbazide hydrochloride, factor 0·7271 (Phillips, *Analyst*, 1923, 367). The last method has the advantage that it can be used to separate vanillin from heliotropin, and in the same paper is described a volumetric process based on the determination of the acidity of an anhydro-derivative,  $(OH)(OCH_3)C_6H_3CH = NC_6H_4CH_3$ , formed by treatment of vanillin with *p*-toluidine. (See under "Vanilla.")

Among the adulterants found in vanillin may be mentioned benzoic acid, which is easily detected by the increased acid value, and acetanilide, which reduces the melting point, and is readily detected by the carbylamine reaction after boiling with potash. Traces of acet-isoeugenol due to imperfect purification during manufacture will give a cherry red colour when the sample is mixed with a few drops of concentrated sulphuric acid.

*Derivatives.*—Bromovanillin, a crystalline substance, melting point 160° to 161°; iodovanillin, crystalline, melting point 174°; vanillin methyl ether, melting point 42° to 43°; vanillin ethyl ether, melting point 64° to 65°; oxime, melting point, 121° to 122°; semicarbazone, melting point 232°; *p*-nitro-phenylhydrazone, melting point 223°; and *p*-brom-phenylhydrazone, melting point 148°.

W. H. S.

**VANISHING CREAMS.**—These are toilet creams which,



## PERFUMERY

When applied to the skin and gently rubbed in, completely disappear, leaving no greasiness. They are used as emollients, and also applied to the skin prior to the use of face powder, when they serve the useful purpose of preventing the powder from penetrating the pores of the skin. The creams consist essentially of emulsions, and contain very large quantities of water, often 70 to 80 per cent. The emulsification is usually brought about by means of an acid stearine soap, in which only a small proportion of the stearine is saponified, but it may also be assisted by the addition of soap already prepared, either hard or soft. Saponification may be effected with soda, potash, or ammonia, and either the hydroxide or carbonate of the alkali may be used. Soda gives the firmest product, and ammonia the softest, the most satisfactory creams being probably those prepared from potash. The carbon dioxide liberated when the stearine is saponified with carbonated alkali is sometimes difficult to expel completely, and leaves gas bubbles in the cream, so that hydroxides are to be preferred. A small quantity of borax is sometimes added; but it must be remembered that this is an acid salt, and acts as such towards soap, liberating fatty acids. It is sometimes considered desirable to reduce the hardness of the stearine; this may be done by adding a small proportion of oleic acid. Other fatty or waxy substances occasionally admixed are cacao butter, lanolin, spermaceti, soft paraffin, and paraffin wax. These are melted in with the stearine prior to saponification. Glycerin, sometimes in considerable quantity, is a normal constituent of vanishing creams, and as much as 30 per cent. is sometimes met with in American and Continental preparations, but in England the presence of any large amount is not popular.

In the manufacture of the creams the stearine is usually first melted with any addition of oleic acid, lanoline, or other fatty or waxy matter, and the appropriate quantity of alkali, dissolved in hot water to which is added any glycerin, is slowly run in, and the mixture stirred continuously till almost cold, when the perfume is added and thoroughly admixed. Some makers, however, prefer to pour the stearine, either finely powdered, or in the molten state, into the alkaline solution to which the glycerin has already been added. The creams can be satisfactorily prepared in a steam-jacketed, enamelled, glass-lined, or tinned pan, fitted with a mechanical stirrer. On the small scale an egg whisk is sometimes employed to facilitate emulsification. A "saponified" stearine melting at about 55° to 56° is the most suitable for the purpose,

and the usual temperature for admixture of the stearine and alkali is about  $80^{\circ}$  to  $85^{\circ}$ . The mixture should be well stirred and maintained at this temperature for about fifteen minutes, when the steam is turned off, and the cream steadily stirred until it is nearly cold and becomes thick. After adding the perfume, it should then be set aside in a warm place and stirred occasionally for a day or two, which improves its appearance. The great aim of many makers is to secure a pearly or satiny appearance rather than a dead white, and this is dependent both on the composition of the cream and the extent of stirring it is subjected to. Too vigorous and prolonged stirring tends to give a dead white effect, but stirring at intervals for a few days after manufacture helps to increase the satiny appearance. The proportion of stearine is usually about 12 to 16 per cent., but up to 20 or 25 per cent. is sometimes employed, though the latter figure should not be exceeded. The amount of alkali added is generally only sufficient to saponify about one-third of the stearine, the remainder, of free stearine, having an emollient effect on the skin, and the pearly appearance has been attributed to the light reflected from the minute crystals of free stearine suspended throughout the mass. If a very stiff cream is required, this can be produced by the addition of gelatine or of a mucilage of starch, gum tragacanth, agar-agar, Irish moss, or quince. The addition of zinc oxide or other insoluble powder is not to be recommended, as it tends to spoil the emulsification.

There are three defects to which these creams are liable: (1) failure to vanish completely when rubbed into the skin, but rubbing up into small dough-like rolls; (2) tendency for the emulsion to separate; and (3) tendency for some of the water to evaporate. As regards the first, a soda cream is much more liable to this defect than one made from either potash or ammonia. On the other hand, a soda cream is much the most stable of the three. Tendency to separation is much reduced by the presence of the various mucilages referred to above, and the addition of glycerin, if in any considerable quantity, helps to retard loss of water by evaporation. To avoid this entirely, however, the cream must be packed in as air-tight receptacles as possible, for which purpose covering with waxed paper, a very thin collodion membrane, or a disc of cardboard impregnated with hard paraffin wax, is often resorted to.

By beating air into creams of this type a white, opaque, and somewhat foamy mass is obtained, which is often slightly medi-

cated, and sold under the name of "snow." Well-known products of this kind are *witch hazel snow*, containing 30 per cent. distilled solution of *hamamelis* in place of some of the water ordinarily added, *camphor snow*, with about 1·5 per cent. flowers of camphor incorporated, and *peroxide snow*, a cream to which 5 per cent. of hydrogen peroxide (20 volumes) is added as it is getting cold.

W. H. S.

**VERBENA, OIL OF.**—The true *verbena* oil must not be confused with the lemongrass oil of commerce, which, on account of its similarity of odour, is frequently called *verbena* oil. (See "*Lemongrass Oil*." )

Nor must the plant from which it is obtained be confused with *Verbena officinalis*, which is practically odourless. This confusion has long existed, and the veneration in which the ancients held *verbena* is sometimes erroneously referred to *Verbena triphylla*, the sweet-scented plant, instead of, properly, to the odourless *Verbena officinalis*. E. M. Holmes (*P. & E. O. R.*, 1913, 284) refers to Sowerby's "*English Botany*," 1866, vol. vi., p. 202, where the following interesting reference to the latter plant occurs:—

"The vervain (*Verbena officinalis*) is a plant with a curious and interesting history. It was undoubtedly the *herba sacra* of the ancient Druids, in honour of which *Verbenalia* were held, and one of the several plants which were dedicated to the service of the altar and the decoration of the priesthood. In ancient Greece the plant was supposed to possess extraordinary virtues. Medea used *verbena* when she gave youth again to Æson, and in Virgil it is stated that the priests bound it about their temples on the morning of the death of Æneas. Vervain was usually offered as a pledge of good faith between the Romans and their enemies, as in the solemn league between Tullus Hostilius and the Albans, and was undoubtedly regarded in the same manner as is a modern flag of truce.

"Mason describes its use in the solemn incantation of the Druids thus:—

'Lift your boughs of vervain blue  
Dipt in cold September dew,  
And dash the moisture chaste and clear  
O'er the ground and through the air.  
Now the place is purged and pure.'

"Something of the superstition of these early times with respect to this plant was transmitted to our more recent forefathers, who regarded it as a charm for many diseases. In Germany and many

## PERFUMERY

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## P E R F U M E R Y

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## P E R F U M E R Y

parts of France it was gathered with many unintelligible cabalistic ejaculations during certain phases of the moon, and was supposed to be a certain charm against witchcraft, and to work miracles of a surprising kind."

The true verbena is *Lippia citriodora* (*Verbena triphylla*; *Aloysia citriodora*), which is probably a native of Chile, and is cultivated in the south of France, where a certain quantity of the essential oil is distilled from the leaves

A certain amount of "Spanish" verbena oil is met with, and until recently was believed to be derived from the same plant. In 1912, however, authentic specimens of the plant, which is commonly called the thyme-lemon plant, were obtained from Spain by J. C. Umney, and carefully examined by E. M. Holmes (*Perfumery Record*, 1912, 212), who definitely identified it as *Thymus hyemalis*, a plant belonging to the natural order *Labiatae*.

The fresh leaves of the true French verbena yield from 0.07 to 0.2 per cent. of essential oil, having a far more delicate odour than ordinary lemongrass oil. Gildemeister and Hoffmann ("The Volatile Oils," vol iii, 2nd ed.) give the following recorded characters for a number of oils, the Spanish oils included —

| Origin.       | Specific gravity. | Optical rotation. | Citral. Per cent. |
|---------------|-------------------|-------------------|-------------------|
| 1. Grasse     | 0.900             | — 12° 38'         | 35                |
| 2. "          | 0.902             | — 12° 7'          | 28                |
| 3. "          | 0.919             | — 16° 20'         | 29.8              |
| 4. "          | —                 | — 14° 16'         | 35.4              |
| 5. "          | —                 | —                 | 65-70             |
| 6. "          | 0.912             | — 15°             | 37.5              |
| 7. "          | 0.905             | — 12°             | 26                |
| 8. "          | 0.918             | — 16°             | 21                |
| 9. "          | 0.905             | — 12° 30'         | 26                |
| 10. Spain     | 0.928             | + 2° 45'          | 13                |
| 11. "         | 0.901             | + 18° 30'         | 20                |
| 12. "         | 0.9085            | + 9° 45'          | —                 |
| 13. "         | 0.9239            | — 5° 25'          | 30                |
| 14. Australia | 0.894             | — 16°             | 74                |
| 15. "         | 0.881             | — 6°              | —                 |

It may be taken for certain that samples recorded under No. 5 (above), containing 65 to 70 per cent. of citral, were not genuine oils, but contained lemongrass oil. A pure verbena oil from the

## P E R F U M E R Y

leaves of *Lippia citriodora* has characters which rarely fall outside the following limits :—

|                            |                 |
|----------------------------|-----------------|
| Specific gravity . . . . . | 0.900–0.920     |
| Optical rotation . . . . . | — 10° to — 18°  |
| Citral . . . . .           | 20–38 per cent. |

The botanical source of the Australian oil is not known with certainty. The principal odorous constituent of it is the aldehyde citral. According to Theulier (*Bull. Soc. Chim.*, 1902, iii., 27, 1113), the French oil also contains limonene, geraniol, a sesquiterpene, and a paraffin hydrocarbon.

E. J. Parry and C. T. Bennett (*Chemist and Druggist*, 1906, 69, 481) reported on a sample of Spanish oil of known authenticity, and stated that it was an oil having an odour of thyme as well as of the aldehyde citral. It had the following characters :—

|   |              |
|---|--------------|
| Specific gravity . . . . .                                    | 0.901        |
| Optical rotation . . . . .                                    | + 18° 30'    |
| Aldehydes . . . . .   | 20 per cent. |
| Amount absorbed by caustic potash .                           | 10 "         |
| Refractive index . . . . .                                    | 1.4808       |
| Refractive index of first 10 per cent.<br>distilled . . . . . | 1.4779       |
| Refractive index of last 20 per cent.<br>(residue) . . . . .  | 1.4980       |

On fractionation the following fractions were obtained :—

|                               |              |
|-------------------------------|--------------|
| Below 175° . . . . .          | None.        |
| Between 175°–180° . . . . .   | 10 per cent. |
| „ 180°–190° . . . . .         | 13 „         |
| „ 190°–200° . . . . .         | 11 „         |
| „ 200°–210° . . . . .         | 12 „         |
| „ 210°–220° . . . . .         | 18 „         |
| „ 220°–230° . . . . .         | 18 „         |
| Residue, above 230° . . . . . | 18 „         |

Charabot and Pillet found that the oil from dried Spanish leaves (0.184 per cent.) had an optical rotation — 10° 30'. They also found that the oil from the Spanish flowers (0.878 per cent.) had an optical rotation + 6° 50', and contained 70 per cent. of citral and about 10 per cent. of alcohols (phenols ?).

*Messrs. Roure-Bertrand Fils* have compared the oils distilled from the true (French) verbena in Grasse, from the leaves and inflorescences respectively. These had the characters given in the table on p. 816.

From the roots they obtained 0.014 per cent., and from the

## P E R F U M E R Y

stems 0.007 per cent., of essential oil (*Bulletin, Roure-Bertrand Fils*, April, 1906, 38).

|                             | Leaves.       | Inflorescences. |
|-----------------------------|---------------|-----------------|
| Yield per cent . . . . .    | 0.195         | 0.132           |
| Optical rotation . . . . .  | — 14° 16'     | — 8° 24'        |
| Esters . . . . .            | 3.5 per cent. | 3.2 per cent.   |
| Combined alcohols . . . . . | 2.8 „         | 2.5 „           |
| Free alcohols . . . . .     | 16.5 „        | 13.8 „          |
| Citral . . . . .            | 35.4 „        | 29.6 „          |

Kerschbaum (*Berichte*, 1900, **33**, 886) isolated from the Spanish oil about 1 per cent. of a ketone,  $C_{10}H_{16}O$ , which he termed verbenone (*q.v.*). Schimmel & Co. (*Report*, October, 1913, 105) also examined a Spanish oil (No. 13 quoted in the table above given), and found it to contain *larvo*-limonene, eucalyptol, citral, verbenone, methyl-heptenone, *d*-citronellol, an alcohol,  $C_{10}H_{18}O$ , having a characteristic odour of citronellol and borneol (which may be identical with the alcohol of this formula found in cypress oil), and probably caryophyllene and a sesquiterpene alcohol.

Verbena oil is used to a considerable extent in perfumery, and is a great favourite in bath preparations, such as bath soap and water softeners. For cheap varieties lemongrass oil is used, but the more delicate odour of the oils described above is preferred for the more expensive preparations.

According to Bert (*Comptes Rendus*, 1923, 550), cymylacetic aldehyde, a compound of the formula  $(CH_3)_2CH.C_6H_4.CH_2.CHO$ , is obtained by condensing magnesium cymyl chloride with ethyl orthoformate, hydrolysing the product with dilute sulphuric acid, and separating the aldehyde by means of its bisulphite compound. It is a pale yellow oil boiling at 243°, having a marked odour of verbenone.

**VERBENONE.**—This body is an odorous ketone found to a small extent in the Spanish, and possibly in the French, oils of verbenone. (See "Verbena Oil.") It is an oil of the formula  $C_{10}H_{14}O$ , and has the following characters:—

|                                   |           |
|-----------------------------------|-----------|
| Boiling point at 16 mm. . . . .   | 103°–104° |
| Specific gravity at 17° . . . . . | 0.974     |
| Refractive index . . . . .        | 1.4995    |
| Optical rotation . . . . .        | + 66°     |

The preparation on which these figures were determined by



Kerschbaum (*Berichte*, 1900, 33, 886) was possibly contaminated with terpenes. The ketone yielded a semicarbazone melting at 208° to 209°.

Verbenone also results from the auto-oxidation of American oil of turpentine. This is in the dextrorotatory form, whilst that present in verbena oil is levorotatory. Pure verbenone regenerated from its semicarbazone has the following characters:—

|                                 |           |
|---------------------------------|-----------|
| Boiling point . . . . .         | 227°–228° |
| Boiling point at 16 mm. . . . . | 100°      |
| Specific gravity . . . . .      | 0.981     |
| Optical rotation . . . . .      | + 61° 20' |
| Melting point . . . . .         | + 6.5°    |
| Refractive index . . . . .      | 1.4993    |

For the constitution of verbenone, see *Roure-Bertrand Fils, Bulletin*, October, 1913, 134

**VETIVENOL.**—There are at least two isomeric sesquiterpene alcohols of this name occurring in oil of vetiver. The alcohols have the formula  $C_{15}H_{24}O$ , and occur both in the free state and in the form of esters. (See "Vetiver Oil.")

**VETIVERT.**—Oil of vetiver (also known as *Cus Cus* or *Khas Khas*) is obtained by the distillation of the roots of *Vetiveria zizanioides* (formerly known as *Andropogon muricatus*), a plant growing freely in India, Ceylon, and also cultivated in certain parts of India, in the Malay territory, the West Indies, Brazil, Java, Réunion, the Philippines, the Seychelles, and elsewhere. As the botanical relationships of this plant have fairly recently been thoroughly examined by Stapf, in common with those of the other grass oils of India, it will be of interest to reproduce his report on the plant (*Kew Bulletin*, No. 8, 1906). Stapf's statement is as follows:—

# 11. VETIVERIA ZIZANIOIDES, Stapf.

(*Andropogon muricatus*, Retz.)

*Khas Khas* (Hind. ?). *Vetiver* (Tamil).

*Early History.*—If we admit certain deductions of the Sanscritists—and there is no objection to them from the botanist's point of view—this grass, best known as *Khas Khas* or *Vetiver*, must have been popular with the peoples of Northern India for a very long time. W. Jones ("Asiat. Research," 1795, vol. iv., p. 306), as long ago as 1795, identified the *Usira* of Kālidāsa with *Khas Khas*, and Hessler ("Susruta's Ayurvedas," 1850, vol. iii.,

p. 174) did the same, whilst among the more recent interpreters of Sanscrit plant names Dutt ("Mat. Med. Hind.," 1900, p. 321) has come to the same conclusion. Other Sanscrit names which have been interpreted in the same sense are *Virana*, *Lámajjaka* (or *Lamaja*), and *Bálá*. According to the "Pharmacographia Indica" (vol. iii., p. 571), "In Vedic times the ancient Hindus were instructed to build their houses in a place where the *Virana* and *Kusa Desmosachya bipinnata* (Stapf) were abundant." *Lámajjaka* is, in the same work (p. 562) referred to "camel's hay" (*C. Schœnanthus*), but the synonyms *Dirgha mulaka* (long-rooted) and *Jalasáya* (aquatic), with which *Lámajjaka* is connected in the Nighandas, are much more descriptive of *Khas Khas*, and Heyne's ("Tracts Hist. Stat. India," 1814, p. 130) and Elliot's ("Fl. Andh.," 1859, p. 106) interpretation of the term as connoting the latter is, therefore, more plausible. Hessler also renders the *Bálá* of Susruta with *Andropogon muricatus*. According to Dutt (*loc. cit.*, p. 293), it stands for *Paronia odorata*, another plant whose aromatic roots are frequently used in Hindu medicine. But the fact that *Bálá* in Hindi actually also denotes the roots of *Khas Khas*, and that the Bengali, Gujerati, and Mahrati synonyms *Válá* and *Valo* are applied in the same sense, supports Hessler's identification. In proof of the assumption that *Khas Khas* was an article of some importance long ago, the authors of the "Pharmacographia Indica" (vol. iii., p. 572) also refer to the discovery of some copper plates in the village of Basahi, in the district of Etawah, south-east of Agra, it being stated that on these copper plates, which are dated A.D. 1103 and 1174, the grass is mentioned among the articles subject to royalties. The actual term used is *turushkadanda*, which Babu Rájendralála Mitra (*Jour. As. Soc. Beng. (Hist. and Lit.)*, 1873, vol. xlii., p. 320; *Proc. As. Soc. Beng.*, 1873, p. 161) interprets as meaning "aromatic reed" (*turushka* = aromatic substance, *danda* = stick), and hence also *Khas Khas*. The latter term, now so commonly used, is supposed to be of Persian origin, but this appears to me very doubtful. It is mentioned in the "Makhzan-el-Adwiyah" (see Dymock, Warden, and Hooper, "Pharmacographia Indica," 1893, vol. iii., p. 572) as a kind of *Izkhir* used in India, also known as *Izkhir-i-Jami* (*Izkhir-i-Ajami*, foreign *Izkhir*), and called by the Persians *bikh-i-wála* (*wála* root).

The *Khas Khas* was long ago equally well known to the Dravidic peoples of the south. Rheede (*Hort. Malab.*, 1703, vol. xii., tab. 72) described and figured the grass under the Malayalam

name *Ramacciam*, which is still in use in Travancore (*Ramacham* Moodeen Sherif; *Ramaccam* Stolz). He states that the roots (but not the leaves) are fragrant, and sold in the bazaars for medicinal purposes to prepare lotions, infusions, and decoctions. It is, he remarks, very common throughout Malabar, and diligently cultivated by the natives, who propagate it by dividing the tufts and planting them in loose soil. He further observes that the best *Ramacciam* grows near Tutocorin, the port which in our own day is still the principal place of export of the roots of *Khas Khas* or *Vetiver*. Rheede's figure represents a leaf tuft with the leaf tops cut off. Although somewhat crude, it is perfectly characteristic, and it is difficult to understand how the *Ramacciam* of the *Hortus Malabaricus* could ever have passed—as it so frequently has done—for the “lemongrass.” Hermann (*Mus. Zeyl.*, 1726, p. 51) 1672-1677, also found the roots in similar use at Colombo, in Ceylon, where they were known as *Lumbutschiveru* (*radix odorata*), and the grass itself as *Saxwendara*, which name has survived to the present day. About twenty-five years later, Dr. Bulkeley sent it to Ch. Du Bois from Madras under the Tamil name *Lettyrecr* (— *Vetiver*) the vernacular name by which the grass is best known in Europe. Petiver (“*Mus. Petiv.*,” 1699, No. 559, p. 53) also received specimens of it from Samuel Browne, of Madras, at about the same time, and announced them in his “*Museum*” as “*Gramen Madraspatanum majus cujus locustæ spinulis eleganter armatæ sunt.*” Some of them he sent to Scheuchzer, who from them drew (“*Agrostogr.*,” 1719, p. 103) up one of those classic descriptions which, for completeness and accuracy, remained long unequalled in agrostological literature.

*Foundation of the Species.—Synonymy.*—No notice was taken of Scheuchzer's description or of Petiver's and Du Bois's specimens, and when Linnaeus, about 1770, received the grass from Koenig, he described it (“*Mant. Alt.*,” 1771, p. 183), as something new under the name *Phalaris zizanioides*. Koenig, however, also sent specimens of the grass to Retzius, who published it as *Andropogon muricatus* (“*Observ.*,” vol. iii., p. 43) in 1783. This name, which was suggested by Koenig himself, was subsequently adopted by Roxburgh and most other botanists. More recently, however, it has been replaced by *Andropogon squarrosus*, a name adopted by the younger Linnaeus (Linné Fils, “*Suppl.*,” 1781, p. 433) for a plant also communicated by Koenig, who found it “*circa Zeylonam natans supra stagna profundiora,*” and entirely

distinct from *Andropogon muricatus*. The specimen is still in Linnæus' herbarium, and was correctly identified by R. Brown ("Prodr. Fl. Nov. Holl.," 1810, p. 193) with his *Panicum abortivum*, that is, *Chamaraphis spinescens*, a characteristic floating grass of the Indo-Malayan region. Retzius (*loc. cit.*, 1789, vol. v., p. 21) himself is responsible for the erroneous reduction of *Andropogon squarrosus* to *Andropogon muricatus*, which recently has been revived, although Roxburgh ("Fl. Ind.," ed. Carey and Wall., 1820, vol. i., p. 270) long ago drew attention to the confusion. "*Zizanioides*" being the earliest specific epithet, it will have to be adopted for the *Khas Khas*, so that its name under *Vetiveria* must be *V. zizanioides*.

*Uses of the Roots.*—Koenig, in a note reproduced by Retzius, remarks: "Tamulis Wœtiwær. Radices ab indigenis usitatissimæ ob gratum odorem quem aqua irroratæ spargunt. Ex his *Flabella* præcipue parantur quæ pennis Pavonum ornantur." This property of the roots of *Khas Khas* of emitting a pleasant odour as often as they are wetted and as long as they are wet was also mentioned by Jones ("Asiat. Research, 1795, vol. iv, p. 306) in 1795. It has led from early times to their being woven into screens and mats (*tatties*), which are hung over doors or set in windows; in hot weather, when frequently sprinkled with water, they cool and perfume the air. The fans (Tamil *visri*) mentioned by Koenig act in the same way. The root, in the powdered state, enters into the composition of an *Abir* ("Dict. Econ. Prod. India," 1885, vol. i., p. 7), or perfumed powder used by the Hindus at the *Hoh* festival. Such an *Abir*, *Abu Izkhir*, is already mentioned in the "Ain-i-Akbari"—the Annals of the Emperor Akbar, (Hooper, in *Calcutta Review*, October, 1904) the appellation *Izkhir* standing here for *Izkhir-i-Ajami*, that is, *Khas Khas*. The *Schænanthus* powder which Herbert de Jager found in use at Golconda in the second half of the seventeenth century was also most likely *Khas Khas* powder. For what he says is this: "In Golkonda, this *Schænanthus* is used in powder form for washing the hands on account of the very pleasant odour it imparts very quickly to the water; but the odour ceases as soon as the hands are dry."

While, however, the use of the roots of *Vetiveria zizanioides* for medicinal purposes and in perfumery has been universal in India for a very long period, I have failed to find, among the earlier writers, any definite and indisputable reference to the extraction of an oil from them. It is true that Hessler, in his

translation of Susruta, mentions (vol. i., p. 160) "*Andropogi muricati spiritus distillatus*"; but the word which he renders as "*Andropogi (sic) muricati*" is *Mrinala*, which by others, as for instance by Dutt, is interpreted as meaning the leaf stalk of the lotus, so that for this reason alone the passage quoted cannot be adduced as proof of an early knowledge of the distillation of oil from *Khas Khas* or *Vetiver*. Indeed, the distillation of *Vetiver* oil in India seems to be of very limited extent, and there is hardly any export, the oil being mainly produced in European distilleries from the imported root; but even the import of the roots as a regular article of commerce appears to be of comparatively recent date.

*Natural Area and Cultivation.*—The natural area of *Andropogon muricatus* in India and Ceylon includes practically the whole country, in the north up to altitudes of 600 metres. Although common in many parts of the country, particularly on the banks of rivers and in rich marshy soil, it is also at present, as in Rheede's time, occasionally cultivated, as, for instance, in Rajputana and in Chutia Nagpur. Eastwards the area extends into Burma. Throughout the Malayan region, however, it occurs only in the cultivated state, or as an escape from gardens. It has also been introduced into the Mascarenes, the West Indies, and Brazil; but it seems that in these countries oil is not distilled to any appreciable extent, except perhaps in Réunion, where the grass must have been in cultivation for at least 100 years, as the first sample of vetiver oil that was chemically examined (in 1809) came from there.

Vetiver requires a warm, damp climate, with an average temperature about 25°, and a firm sandy and clayey soil. The plant is propagated by cutting off fragments of the roots and transplanting them. Well-cultivated land will yield about 2½ tons of marketable clean roots per hectare.

Puran Singh has examined seven samples of the root obtained from different localities, with the results given in the table on p. 822.

The distillation of the essential oil is somewhat difficult, as it has a very high boiling point, so that up to the present not a great deal is distilled in India. A large quantity of the root is exported, and this is distilled in Europe. The oil distilled in Réunion differs from that distilled in Europe, partly on account of the greater freshness of the Réunion roots, and partly on account of the methods of distillation.

## P E R F U M E R Y

The essential oil is a thick, brownish, very viscid liquid with an intense and persistent odour, which renders it suitable for heavy so-called Oriental perfumes, and also of considerable value as a

|   | Moisture.<br>Per cent. | Ash per cent.<br>on dry<br>matter. | Essential oil.<br>Per cent. |
|---|------------------------|------------------------------------|-----------------------------|
| 1. Godhra Range . . . . .               | 8.51                   | 2.66                               | 0.72                        |
| 2. Ajmer, Rajputana . . . . .           | 10.14                  | 3.1                                | 1.13                        |
| 3. Pilibhit, United Provinces . . . . . | 10.46                  | 4.3                                | 0.69                        |
| 4. " " " " " . . . . .                  | 9.51                   | 4.71                               | 0.37                        |
| 5. Belgaum Forest Division . . . . .    | 10.88                  | 3.84                               | 0.99                        |
| 6. Yeomatal Forest Division . . . . .   | 9.45                   | 3.1                                | 0.45                        |
| 7. Delhi . . . . .                      | 9.81                   | 2.17*                              | 1.14                        |

perfume fixative. The oil distilled in Europe has the following characters :—

|   |                |
|---|----------------|
| Specific gravity . . . . .              | 1.014–1.040    |
| Optical rotation . . . . .              | + 25° to + 38° |
| Refractive index . . . . .              | 1.5210–1.5270  |
| Acid value . . . . .                    | 27–65          |
| Ester value . . . . .                   | 10–25          |
| Ester value after acetylation . . . . . | 130–160        |

The oil is soluble in 1 to 2 volumes of 80 per cent. alcohol, the addition of more alcohol causing turbidity.

This oil is not often adulterated, but sometimes artificial esters, principally glyceryl acetate or benzyl benzoate, are found present, and should be searched for.

The oil distilled in Réunion usually has a lower specific gravity than that distilled in Europe. Its characters are as follows :—

|   |                |
|---|----------------|
| Specific gravity . . . . .              | 0.980–1.020    |
| Optical rotation . . . . .              | + 15° to + 37° |
| Refractive index . . . . .              | 1.5150–1.5280  |
| Acid value . . . . .                    | 4–20           |
| Ester value . . . . .                   | 5–20           |
| Ester value after acetylation . . . . . | 105–146        |

The solubility of the oil in 80 per cent. alcohol is the same as that of the European-distilled oils.

Puran Singh (*Chemist and Druggist*, 1914, 85, 225) gives the

## P E R F U M E R Y

Following figures for a sample distilled in India, and rectified by means of steam distillation :—

|   |          |
|---|----------|
| Specific gravity . . . . .              | 1.011    |
| Optical rotation . . . . .              | — 30.65° |
| Refractive index . . . . .              | 1.5165   |
| Acid value . . . . .                    | 10.5     |
| Ester value . . . . .                   | 69.6     |
| Ester value after acetylation . . . . . | 132.8    |

The levorotation was due to the fact that the resinous matter which remained in the still was highly dextrorotatory (+ 488°). Commercial distillates, however, always contain this resinous matter, and are dextrorotatory.

*Roure-Bertrand Fils (Bulletin, April, 1914)* have distilled vetivert roots produced in the Philippines, with the following results :—

On submitting 197 kg. of these roots to distillation, they extracted from them 1.340 kg. of direct essential oil, and by exhausting the condensed waters by means of light petroleum spirit, after using this solvent for rinsing out the various distillation utensils, they obtained a further quantity of 0.475 kg. In all, therefore, they obtained 1.815 kg. of volatile oil, which brings the total yield up to 0.92 per cent.

Below are the principal characters of this product, determined on the direct essential oil. —

|   |                    |
|---|--------------------|
| Specific gravity . . . . .  | 1.0139             |
| Optical rotation . . . . .  | + 30° 8'           |
| Rotation of the acetylated oil . . . . .                                | + 12° 32'          |
| Decrease in rotation . . . . .  | 17° 36'            |
| Solubility in 80 per cent. alcohol . . . . .                            | 0.75 vol. and over |
| Acid value . . . . .  | 21.5               |
| Coefficient of saponification . . . . .                                 | 28.0               |
| Ester value . . . . .   | 6.5                |
| Proportion of ester (acetate of an alcohol, $C_{15}H_{24}O$ ) . . . . . | 3.0 per cent.      |
| Coefficient of saponification after acetylation . . . . .               | 165.2              |
| Combined alcohols, $C_{15}H_{24}O$ . . . . .                            | 2.5 per cent.      |
| Free alcohols . . . . .   | 74.5 „             |
| Total alcohols . . . . .  | 74.0 „             |

Bacon describes the oil of *Andropogon squarrosus* (?), which grows freely in the Philippines, where it is known as vetivert ; the oil, however, does not resemble vetivert at all in odour (*Philipp. Jour. Science*, 4, 93).

## P E R F U M E R Y

Georgi (see *P. & E. O. R.*, 1924, 289) has distilled the oil from roots grown on the Government experimental plantations at Serdang, but at present the oil is not distilled on a commercial scale in Malaya. The oil was examined at the Imperial Institute, and was found to have the following characters :—

|   |        |
|---|--------|
| Specific gravity . . . . .              | 1.032  |
| Refractive index . . . . .              | 1.5240 |
| Acid value . . . . .                    | 35.5   |
| Ester value . . . . .                   | 11.8   |
| Ester value after acetylation . . . . . | 162    |

An oil distilled in the Fiji Islands was examined at the Imperial Institute (*Bull. Imp. Inst.*, 1912, 10, 32). It was of a dark green colour, and had a specific gravity 1.0298, and an acid value 35.3.

The constituents of vetivert oil are, at present, not completely understood. According to Franz Fritzsche & Co. (German Patent 142415 of 1902), the oil is, in the main, composed of a mixture of ketones, which they termed vetirone or vetiverone, having the empirical formula  $C_{11}H_{22}O$ , and probably consisting of several isomers, which boil at about  $150^{\circ}$  at 10 mm. and have a specific gravity about 0.990. They also state that there are present two alcohols, which, although of different formulæ, they named vetirols or vetiverols, and which had the following characters :—

|                                  | 1.                            | 2.                            |
|----------------------------------|-------------------------------|-------------------------------|
| Formula . . . . .                | $C_9H_{14}O$                  | $C_{11}H_{18}O$               |
| Boiling point at 10 mm . . . . . | $150^{\circ}$ – $155^{\circ}$ | $174^{\circ}$ – $176^{\circ}$ |
| Specific gravity . . . . .       | 0.980                         | 1.020                         |

Genvresse and Langlois (*Comptes Rendus*, 1902, 135, 1059) examined the oil, and claimed to have isolated a sesquiterpene,  $C_{15}H_{24}$ , which they named vetivene, a colourless oil having no odour, boiling at  $263^{\circ}$  at 740 mm., of specific gravity 0.932 at  $20^{\circ}$ , and optical rotation  $+18^{\circ} 19'$ . They also claimed to have isolated another odourless constituent from the oil which was a sesquiterpene alcohol, which they named vetivenol. This body is described as a viscid, pale yellow, odourless oil boiling at  $169^{\circ}$  to  $170^{\circ}$  at 15 mm., having a specific gravity 1.011 at  $20^{\circ}$ , and optical rotation  $+53^{\circ} 43'$ . On dehydration by means of oxalic acid, this alcohol yields the sesquiterpene vetivene. According to Genvresse and Langlois, the odour bearer of vetivert oil is the ester of this alcohol, vetivenol, with an acid (or mixture of acids) of the empirical formula  $C_{15}H_{24}O_4$ . Schimmel & Co. (*Bericht*, April, 1899, 50) have found crystals of zinc palmitate in a vetivert



which had been kept for some time in a zinc container, and consider that palmitic acid is a constituent of the oil.

Bacon (*Philipp. Jour. Sci.*, 1909, 4, 118) does not agree with the views of Genvresse and Langlois, since the oil, when saponified, retains a masked vetiver odour, which the latter chemists ascribe to the ester, stating that the free alcohol is odourless. Bacon obtained a considerable amount of benzoic acid on the saponification of the oil.

The most reliable and authoritative work on this oil appears to be that of Semmler, Risse, and Schröter (*Berichte*, 1912, 45, 2347). These chemists examined an oil distilled by *Schimmel & Co.*, which had the following characters: specific gravity at 20°, 1.0239; optical rotation, + 31°; and refractive index, 1.5255. Four hundred grams were fractionated at 12 mm., with the following results:—

|                        |           | Per cent. |
|------------------------|-----------|-----------|
| Fraction A, boiling at | 129°–175° | 23        |
| „ B „                  | 175°–190° | 34        |
| „ C „                  | 190°–250° | 8         |
| „ D „                  | 250°–300° | 30        |

Fraction D was resolved into two fractions as follows:—

|                          | Per cent. |
|--------------------------|-----------|
| Da, boiling at 138°–260° | 28        |
| Db, „ 260°–298°          | 62        |

The fraction Da was found to consist of an ester,  $C_{30}H_{44}O_2$ , the constituent elements being an alcohol,  $C_{15}H_{24}O$ , and an acid,  $C_{15}H_{22}O_2$ . The alcohol, which appears to be the vetivenol of Genvresse and Langlois, has the following characters: boiling point, 170° to 174° at 13 mm.; specific gravity at 20°, 1.0209; optical rotation, 1.52437; and molecular refraction, 66. Vetivenol is therefore probably a tricyclic sesquiterpene alcohol with only one double linkage. The acid,  $C_{15}H_{22}O_2$ , has been named vetivenic acid. It boils at 202° to 205° at 13 mm.

Fraction C yielded a mixture of isomeric sesquiterpene alcohols, including the tricyclic vetivenol above described, and a dicyclic vetivenol. This fraction also contained vetivenic acid.

From fraction A two sesquiterpenes were obtained, which are termed vetivene, and which had the following characters:—

|                         | Tricyclic<br>vetivene. | Dicyclic<br>vetivene. |
|-------------------------|------------------------|-----------------------|
| Boiling point at 16 mm. | 123°–130°              | 137°–140°             |
| Specific gravity at 20° | 0.9355                 | 0.9321                |
| Optical rotation        | + 2° 16'               | – 10° 12'             |
| Refractive index        | 1.51126                | 1.51896               |

## PERFUMERY

The same chemists examined an oil distilled in Réunion, which had a specific gravity 0.9916 at 20°; optical rotation, + 24° 6'; and refractive index, 1.52429; and a second oil, of specific gravity 0.9982 at 20°; optical rotation, + 31°; and refractive index, 1.52517. In these oils very little of the vetivenol ester of vetivenic acid was found, but both the isomeric vetivenols and the vetivenes were present.

Vetivert oil is used to a considerable extent in high-class perfumery.

**VIOLET, THE ODOUR OF.**—See also "Ionone."—Few perfumes are more popular than that of the violet. But the violet perfume as it has been placed before the public has had some vicissitudes, and the popular taste of to-day is not that of yesterday, and possibly will not be that of to-morrow. The perfume was originally valued for its real resemblance to the perfume of the natural flowers. Then came the discovery of ionone and its relations, and the powerful violet-like odour of the artificial perfume ousted the sweet, delicate, and much more expensive perfume derived from the flower. To day the bulk of the "violet" perfume offered to the public is purely artificial, consisting entirely of ionone or its derivatives. A small proportion is a mixture of the artificial and natural products, and a minute proportion may be the really natural perfume. But the perfume of a bunch of violets embedded in the green leaves of the plant is far sweeter and more refreshing than that of the flowers by themselves. This "violet-leaf" perfume, added to that of the "violet flower," has also been to some extent matched synthetically by compounds of the methyl-heptine-carbonate type (*q.v.*). Thus the manufacture of artificial violet perfumes has been brought to a high degree of perfection, and no branch of the perfumer's art is more dependent on artificial products than the manufacture of the violet odour.

The flower *Viola odorata* is a native of Europe, and is found in the woods, groves, and hedges throughout nearly all European countries, and also in Siberia, China, and Japan. There are a number of varieties of this species of *Viola*, nearly all of which are beautifully scented. Of these the following are the principal:—

(1) Var. *vulgaris*. The flowers are, according to Sawer ("Odorographia," i., 104), deep purple or purplish-blue, pale and streaked in the mouth. The perfume is very delicate.

(2) Var. *cœrulea*. The flowers are blue and very delicate in odour.

## P E R F U M E R Y

- (3) Var. *purpureo-plena*. The flowers are purple, and double.
  - (4) Var. *cœruleo-plena*. The flowers are blue, and double.
  - (5) Var. *pallido-plena*. The flowers are pale blue, and double.
- This variety is usually termed the Neapolitan violet.
- (6) Var. *alba*. The flowers are white. It is very plentiful in Surrey.
  - (7) Var. *albo-plena*. The flowers are white, and double.
  - (8) Var. *variegata*. The flowers are variegated.
  - (9) Var. *cornuta*. The flowers have horned petals.

The habit of growth of all these varieties is trailing. There are nearly 200 species of *Viola*, of which some others than *Viola odorata* are scented : but those principally cultivated in the south of France for their perfume are the double purple and double blue varieties of *Viola odorata*, especially the Neapolitan violet, and varieties known as "Victoria" and "Prince of Wales" (*but see below*). According to the *Perfumery and Essential Oil Record*, 1916, 315, the young plants are usually planted out in the rainy season, generally in October. The ground is previously broken up and well manured, and the plants are placed in furrows. The most suitable place is in the olive groves, where they are well protected from the sun's rays in summer and from the extreme cold in winter. Flowering commences towards the end of November, and in December the leaves are almost overshadowed by the flowers, which then bloom in profusion. The flowers are picked twice a week, as they lose their perfume if allowed to remain on the plant, and must all be gathered before they become overgrown with leaves. They are collected in the morning and taken to the factories in the afternoon, as they rapidly lose their perfume when picked. The plants are somewhat delicate, and their harvest is subject to various climatic influences. Every four or five years the old plants are removed and young roots substituted and placed between the old rows. The second year's growth is the most productive.

• The violet may be propagated by means of seeds, by stolons or runners, and separation of tufts. The suckers are separated from the mother plant from January to March, and planted in rows 50 cm. apart, with a space of 25 to 30 cm. between the plants. Towards the end of June each year the lower parts of the plants are banked up, and if much exposed to the sun, they are covered with brambles.

The violet always requires good manure, and in the autumn liquid human manure is beneficial. Every year, after flowering,

## PERFUMERY

the young shoots which are detrimental to the development of tufts are removed.

There are several distinct varieties of *Viola odorata*, the colour of the flowers ranging from white to blue and deep purple. The varieties chiefly cultivated for their perfume are the double purple and double blue varieties. The variety known as "double Parma" is also a favourite.

The perfume is extracted by the hot maceration method, the fat being afterwards washed with alcohol for the production of the triple essence. The volatile solvent method of extraction is now very largely employed for the production of concrete essence and "absolutes." The products obtained by this method are more stable than the pomades, and can be kept indefinitely for dilution with spirits of wine when required.

Extracts of ~~the~~ leaves are also prepared for perfumery and for scenting soaps. These are prepared by the petroleum ether process, and are usually sold in a semiliquid form, green in colour. The addition of this extract to the floral extract or to the artificial product gives a characteristic leaf odour, which greatly improves the bouquet and forms an ideal violet perfume, the odour of which is rendered more lasting. Care, however, should be taken not to use too much.

According to a writer in *Les Parfums de France* (1924, 13, 27), the Parma violet and the Victoria violet, with perhaps a small but diminishing quantity of *violettes des bois*, practically furnish all the natural violet perfume used in commerce. The plants are exhausted after six to seven years' production. He points out that the crops of Victoria violets before the war amounted to about 130,000 kg. per annum, but to-day they come to only about 60,000 kg., of which only 20,000 kg. are employed in perfumery. The principal—indeed, almost the only—variety of the Victoria violet now used in perfumery is *La Luxurieuse*. The varieties Princess of Wales, Wilson, and Czar have almost disappeared from cultivation.

As has been indicated above, the essential oil of the violet flower is not capable of extraction on a commercial scale. The chemistry of the oil is not fully understood, but for the investigation of the allied odours of ionone and irone, see under "Ionone" and "Orris Root."

The leaves of the violet are extracted in the south of France by volatile solvents, and commercial products of the nature of absolutes or concretes are obtained by this process. The perfume

of this leaf extract is so powerful and, on dilution, so attractive that the extract is of the greatest value to perfumers.

The essential oil of violet flowers—of which 1,000 kg. are necessary to produce 31 grams of oil—has been examined by Von Soden (*Jour. Prakt. Chem.*, 1904, ii., 69, 261). It is an oil having a faintly greenish colour, of specific gravity 0.920; optical rotation,  $+104^{\circ} 15'$ ; acid value, 10; and ester value, 37.

*Viola tricolor*, the common pansy, yields, when the whole plant is distilled, 0.0086 per cent. of an essential oil which has a decided odour of wintergreen. The oil appears to consist almost entirely of the ester methyl salicylate, which is derived from a glucoside present in the plant.

Goris and Vischniac (*Bulletin, Roure-Bertrand Fils*, April, 1921, 3) have examined the essential oil of violet roots. They had observed that in certain cases glucosides occur in the roots of plants, and the roots, when properly treated, yield, by decomposition of these glucosides, an essential oil which closely resembles the essential oil of the flowers.

One day, in the country, they were struck by a strong and agreeable violet odour emanating from a hedge at the foot of which there was a thick bed of *Viola odorata*; this was surprising, as the plant was not yet in flower. On closer examination they saw that in pecking the soil some fowls had laid bare the roots of the violet, and had bruised the tissues of the subterranean organ. This gave rise to the odour, which was noticeable at a considerable distance. They repeated the experiment and, on bruising some fresh roots, confirmed their observation. The odour was, however, less agreeable, as it was contaminated with a somewhat stale herbaceous odour.

*Messrs. Roure-Bertrand Fils* placed at their disposal the raw material necessary to carry out the preliminary investigations.

One hundred and twenty-two kilograms of violet roots gathered in March in the Grasse district were sterilised, and afterwards exhausted by boiling alcohol with the addition of carbonate of lime. On distilling the alcohol, an extract was obtained which they treated in the following manner in the laboratory:—

The extract, which was very rich in chlorophyll, was exhausted in portions of 500 grams at a time with moist ethyl acetate. The exhaustion was effected at boiling temperature, and repeated three times for each fraction. The ethyl acetate fractions were mixed and distilled, and the green residue was extracted with hot water. The chlorophyll remained insoluble.

The aqueous solution was filtered and washed eight times with ether, until nothing further was extracted. The ether removed a yellow oil with an aromatic odour.

An aqueous solution of a glucoside and an essential oil were thus obtained.

The oil was examined with the following results :—

*Part Soluble in Benzene.*—This oil is easily soluble in benzene, On evaporation of the benzene solution a crystalline mass was obtained ; it was dissolved in sodium carbonate solution, filtered, and precipitated with hydrochloric acid. On extracting the hydrochloric acid solution with ether and evaporation of the solvent, a crystalline residue was obtained which gave a green coloration with dilute ferric chloride.

*Part Insoluble in Benzene.*—This was saponified with alcoholic potash. The alcohol was distilled, the residue dissolved in water, washed with ether, and the acid liberated by the addition of hydrochloric acid. The solution was extracted with ether, and the ethereal extract dried with anhydrous sodium sulphate, filtered, and distilled. The residue obtained was recrystallised from a small quantity of boiling petroleum ether. Salicylic acid crystals, slightly yellow in colour, were obtained, melting at 152° and giving all the reactions for salicylic acid (violet coloration with ferric chloride, sublimation with phenolic odour, etc.).

The roots contain, therefore, a very small quantity of a salicylic ester, possibly methyl salicylate.

**VITEX AGNUS-CASTUS, OIL OF.**—The leaves of *Vitex Agnus-castus* yield about  $\frac{1}{2}$  per cent. of a brown essential oil having an odour which resembles hyssop. It has been examined by Schimmel & Co. (Report, April, 1908, 121), and found to have a specific gravity 0.901 ; optical rotation,  $-7^{\circ} 55'$  ; acid value, 6.4 ; ester value, 18.3 ; and ester value after acetylation, 58.4. It contains eucalyptol, and probably sabihene and a quinone. An oil distilled by Haensel was stated by him (*Chem. Zentral.*, 1909, 1, 1477) to contain eucalyptol, pinene, palmitic acid, a sesquiterpene, and probably a sesquiterpene alcohol. The seeds yield a similar oil with a decidedly spicy odour.

**VITEX TRIFOLIA, OIL OF.**—The leaves of *Vitex trifolia*, a plant belonging to the natural order *Verbenaceæ*, are used in India for baths, and also in Japan, where the plant is known as *Hamapp*. They yield an essential oil of spicy odour, which, according to the chemists of the Botanical Gardens in Buitenzorg, has a specific gravity 0.884, and optical rotation  $-39.75^{\circ}$ .

Shinosaki (*Jour. Chem. Ind. Japan*, 1921, **24**, 191) examined three samples of the oil distilled in Japan, which had the following characters :—

|                                   |                     |
|-----------------------------------|---------------------|
| Specific gravity . . . . .        | 0.8908 to 0.9141    |
| Optical rotation . . . . .        | 39° 6' to —47° 20'. |
| Refractive index . . . . .        | 1.4707 to 1.5010    |
| Acid number . . . . .             | 0 to 1.75           |
| Saponification number . . . . .   | 23.38–38.7          |
| “ “ “ after acetylation . . . . . | 40.14–53.34         |

The constituents of the oil were found to be *hero-pinene*, camphene, terpinyl acetate, and a diterpene alcohol of the formula  $C_{20}H_{32}O$  or  $C_{20}H_{34}O$ .

**VITIS VINIFERA.**—See “Cognac Oil.”

**WALLFLOWER, OIL OF.**—See “Cheiranthus.”

**WALNUT-LEAF OIL.**—The fresh leaves of *Juglans regia* (N.O. *Juglandacea*) yield about 0.01 to 0.03 per cent. of an aromatic essential oil having an odour recalling that of tea and amber (*Schimmel's Bericht*, October, 1890, 61, *Chem. Zentral*, 1907, ii., 1620). The oil distilled from German leaves has the following characters :—

|                            |                      |
|----------------------------|----------------------|
| Specific gravity . . . . . | 0.9037–0.9137 at 30° |
| Optical rotation . . . . . | ± 0°                 |
| Acid value . . . . .       | 9.3–16.8             |
| Ester value . . . . .      | 18.4–27              |

It is semisolid at ordinary temperatures.

*Schimmel & Co* (*Bericht*, April, 1912, 131) have distilled an oil at Barrême in the south of France. The oil which separated from the distillation water was examined separately, and also the oil extracted from the distillation water by ether. The oils had the following characters :—

|   | Direct oil.<br>83 per cent. | Cohobation oil.<br>17 per cent. | Total oil.      |
|---|-----------------------------|---------------------------------|-----------------|
| Yield . . . . .                         | 0.0072 per cent             | 0.0015 per cent                 | 0.0087 per cent |
| Specific gravity at 30° . . . . .       | 0.9174                      | 0.9231                          | 0.9185          |
| Optical rotation . . . . .              | —17° 36'                    | —16° 12'                        | —17°            |
| Refractive index at 25° . . . . .       | 1.4918                      | 1.4937                          | 1.4922          |
| Acid value . . . . .                    | 3.7                         | 6.7                             |                 |
| Ester value . . . . .                   | 9.3                         | 9.7                             |                 |
| Ester value after acetylation . . . . . |                             |                                 | 98.5            |

## P E R F U M E R Y

With the exception of a solid paraffin hydrocarbon, the constituents of the oil have not been identified.

**WARBURGIA STUHLMANNI.**—The wood of this tree, a native of Zanzibar, yields about  $\frac{1}{2}$  per cent. of essential oil having an odour recalling that of sandalwood oil. It has the following characters :—

|   |               |
|---|---------------|
| Specific gravity . . . . .              | 0.9864 at 20° |
| Refractive index . . . . .              | 1.5127        |
| Optical rotation . . . . .              | — 41.77°      |
| Ester value . . . . .                   | 11.2          |
| Ester value after acetylation . . . . . | 111.5         |

The oil contains aldehydes, esters, and free alcohols, the nature of which has not yet been established. The wood is known in East Africa as *karambaki* wood.

**WARTARA SEED OIL.**—See “Xanthoxylum Oils.”

**WATERMINT OIL.**—See “Mentha Oils.”

**WATTLE BLOSSOM.**—See “Acacia.”

**WEBERA THYRSOIDEA.**—This and several other species of *Webra* are highly odorous plants. *Webra thyrsoides* is a small tree found on the hills of the Deccan Peninsula at altitudes of 2,000 to 6,000 feet. Its flowers are reddish-white and very fragrant. *Webra odorata* is a native of Silhet, Assam, the Khasia Mountains, Muneypoor, Penang, and Prince of Wales Island. These plants are closely allied to *Rondeletia*. (See Sawer, “Odorographia,” ii., p. 460.)

**WINE, OIL OF.**—See “Cognac Oil.”

**WINTERGREEN OIL.**—See “Birch (Sweet), Oil of.”

**WINTER'S GRASS.**—This is a name given to the *Maha pengiri* variety of citronella grass, as it was originally cultivated by a firm named Winter & Son. (See “Citronella Oils.”)

**WITCH HAZEL.**—See “Hamamelis.”

**XANTHORRHŒA OILS.**—The so-called “grass tree gums” of Australia yield, not only resins of commercial value, but also essential oils which, although not used at present on a commercial scale, present considerable possibilities to the perfumer. Several of them yield highly aromatic essential oils having an odour of balsam of Peru, storax, and similar balsamic substances. *Xanthorrhœa hastilis* is the “yellow gum,” and *Xanthorrhœa australis* is



the "red gum." The two essential oils have the following characters:—

|                        | Yellow gum. | Red gum. |
|------------------------|-------------|----------|
| Specific gravity . . . | 0.937 ..    | 0.963    |
| Optical rotation . . . | — 3° 14' .. | ± 0°     |
| Acid value . . .       | 4.9 ..      | 47.6     |
| Ester value . . .      | 69.4 ..     | 37.5     |

Cinnamic acid has been found in both essential oils, and styrol in the red gum oil.

An investigation of the essential oils of several *Xanthorrhœa* species has recently been carried out by Rennie, Cooke, and Finlayson (*Jour. Chem. Soc.*, 1920, 338). In one oil, the botanical source of which could not be verified, the constituent which formed almost the whole of the oil was identified as pæonol,  $C_9H_{10}O_3$ , which is *p*-methoxy-*o*-hydroxyphenyl-methyl ketone. The oil from the oleo-resin of *Xanthorrhœa tateana* contains pæonol and hydroxy-pæonol. The oil from *Xanthorrhœa preissii* contains pæonol, hydroxy-pæonol, and a body which is probably methoxy-diphenyl ether. Traces of *l*-citronellol were also found in the oil.

• **XANTHOXYLUM OILS.**—There are a number of essential oils derived from various species of *Xanthoxylum* (N.O. *Rutaceæ*) having very aromatic odours. From the fruits of *Xanthoxylum piperitum*, also known as Japanese pepper, or as *sansho* in Japan, about 3 per cent. of essential oil is obtained which has, according to Schimmel & Co., an agreeable odour of lemons. Schimmel & Co. (*Bericht*, October, 1890, 61) examined an oil of specific gravity 0.973, and stated that the principal constituent was citral. Duruttis, however (*Arbeit. Pharm. Inst. Univ. Berlin*, 60), states that the oil has the following characters:—

|                               |         |
|-------------------------------|---------|
| Specific gravity at 20° . . . | 0.890   |
| Optical rotation . . .        | — 26.5° |
| Refractive Index . . .        | 1.4732  |

He identified about 90 per cent. of terpenes, limonene being one of them. Cumic aldehyde was found, and geraniol, but no citral.

An oil examined by Asahina and Konno (*Apptheker Zeitung*, 1917, 32, 556) had a specific gravity 0.851 at 19°, and specific rotation + 45.45°. It contained phellandrene and cumic aldehyde.

Whether any of the oils above described were not accurately traced to the botanical source, or whether local conditions are

## P E R F U M E R Y

responsible for the differences between them, is uncertain. The former is, however, the probable explanation of these differences.

Helbing (*Jahresb. f. Pharm.*, 1887, 157 ; 1888, 128) has described the oil from the seeds of *Xanthoxylum Hamiltonianum*, from which from 3·8 to 5 per cent. was obtained. The oil had a specific gravity 0·840, and had a persistent odour recalling that of geranium and bergamot oils.

Shinosaki (*Jour. Soc. Chem. Ind.*, 1915, 34, 1270) has examined three oils distilled from the leaves of *Xanthoxylum ailanthoides* at different stages of development. The oils contained terpenes, a small quantity of phenols, and methyl-nonyl-ketone. They had the following characters :—

|                          | Full grown<br>leave . | Half grown<br>leaves. | Young<br>leaves. |
|--------------------------|-----------------------|-----------------------|------------------|
| Specific gravity . . . . | 0·8437                | 0·8385                | 0·8390           |
| Optical rotation . . . . | — 6° 35'              | — 5° 75'              | — 6° 63'         |
| Refractive index . . . . | 1·4474                | 1·4408                | 1·4440           |
| Acid value . . . . .     | 0·94                  | —                     | 0·04             |
| Saponification value . . | 2·81                  | 4·21                  | 1·83             |

*Schimmel & Co.* (*Bericht*, April, 1900, 49 , October, 1911, 49) have distilled the fruits of *Xanthoxylum acanthopodium*, which are known in India as *Wartara* seeds. According to the “*Pharmacographia Indica*” (vol i , p. 257), this substance has long been used as a spice and a medicament in the East. Sanskrit writers call the carpels of the fruit *Tumburu*, which, literally, means coriander.

Ibn Sina (Gildemeister and Hoffmann, “*The Volatile Oils*,” vol. ii., p. 627) describes it as an open-mouthed (*faghureh*) berry, of the size of a vetch, containing a seed resembling that of the hemp. From the word *faghureh* the genus *Fagara* is obviously derived, and the genera *Fagara* and *Xanthoxylum* are so closely related that they are often considered identical.

*Schimmel & Co.* (*loc. cit.*) obtained 2 per cent. of essential oil with a marked odour of coriander. It had the following characters :—

|                          |                    |
|--------------------------|--------------------|
| Specific gravity . . . . | 0·871 to 0·874     |
| Optical rotation . . . . | +5° 30' to +6° 31' |
| Acid value . . . . .     | 27·1               |

It contained dipentene, *d*-linalol, and methyl cinnamate.

The fruits of *Xanthoxylum alatum* have been offered on the

## P E R F U M E R Y

London market as Chinese wild pepper. Umney (*P. & F. O. R.*, 1912, 37) has examined a sample of the oil, which he found to have a specific gravity 0.889, and optical rotation  $-23^{\circ}$ . It contains a crystalline stearoptene melting at  $80^{\circ}$ . Schimmel & Co. (*Bericht*, October, 1910, 147) obtained from the fruits 3.7 per cent. of oil of a lemon yellow colour, and an odour recalling that of water fennel. On continued distillation a solid substance came over which melted at  $83^{\circ}$ , which is probably identical with Umney's "stearoptene," but purified by recrystallisation. The oil itself had the following characters :—

|                               |           |                   |
|-------------------------------|-----------|-------------------|
| Specific gravity              | . . . . . | 0.8653            |
| Optical rotation              | . . . . . | $-23^{\circ} 35'$ |
| Refractive index              | . . . . . | 1.4813            |
| Acid value                    | . . . . . | 0.9               |
| Ester value                   | . . . . . | 10.3              |
| Ester value after acetylation | . . . . . | 33.6              |

Semmler and Schossberger (*Berichte*, 1911, 44, 2885) isolated a terpene, which they named xanthoxylene, but which, according to Gildemeister and Hoffmann, may be identical with sabinene. The solid substance (stearoptene) is the dimethyl ether of phlor acetophenone,  $C_{10}H_{12}O_1$ . Cuminic aldehyde is also present. It is probable that the stearoptene examined by Semmler and Schossberger is identical with the xanthoxylin of Stenhouse, which he believed he had isolated from the oil of *Xanthoxylum piperitum*, but which was later shown by Hanbury (*Pharm. Jour.*, 1857, 1, 17, 19) to have been derived from *Xanthoxylum alatum*. This plant also grows in China, where it is known as *Rhoa Tchiao*. It is a wild mountain shrub, all parts of which have a powerful aromatic odour. It is imported into the United States for perfumery purposes. It is grown in the provinces of Kouang-Si, Canton, Se-Tchouan, Chen-Si, throughout the south, and is employed as a spice. The leaves are eaten in fritters, and are much appreciated. The seed is utilised as a preservative for furs and in making a lotion for the hair.

*Xanthoxylum Aubertia* is a plant known in Réunion as *Catafille blanc*. The essential oil has the following characters (*Schimmel & Co.*, *Bericht*, April, 1907, 105) :—

|                               |           |  |
|-------------------------------|-----------|--|
| Specific gravity              | . . . . . | 0.905–0.971                            |
| Optical rotation              | . . . . . | $-19^{\circ} 20'$ to $-62^{\circ} 10'$ |
| Acid value                    | . . . . . | 1.1–1.4                                |
| Ester value                   | . . . . . | 7.3–8.7                                |
| Ester value after acetylation | . . . . . | 33–51                                  |

## P E R F U M E R Y

The oil contains an olefinic terpene, a sesquiterpene which has been named evodene, methyl-eugenol, and phloracetophenone dimethyl ether (Semmler and Schosserberger, *loc. cit.*).

The oil from the seed coats of *Xanthoxylum senegalense* (*Fagara Xanthoxyloides*) has the following characters:—

|                   |           |         |
|-------------------|-----------|---------|
| Specific gravity  | . . . . . | 0.9229  |
| Specific rotation | . . . . . | — 1.20° |
| Acid value        | . . . . . | 2.2     |
| Ester value       | . . . . . | 58.5    |

It contains methyl-nonyl ketone, decylic aldehyde (?), dipentene, linalol, a sesquiterpene, esters, and the lactone xanthotoxin. This last-named body was isolated by Thoms, who found it to be a mixture of two substances which, by repeated recrystallisations, was separated into two isomeric bodies of the formula  $C_{12}H_{18}O_4$ , xanthotoxin, melting at 146°, and bergaptene, melting at 191°.

**XIMENIA ÆGYPTICA.**—This plant, also known as *Balanites Ægyptica*, is, according to Pliny ("Nat. Hist.," xiii., 2), one which provided the ingredient "balaninum" of the true spikenard ointment. The genus *Ximenia*, which contains a number of odoriferous species, was named after the Spanish monk Ximenes, who published several works on the medicinal plants of the Spanish colonies.

**XYLENE-MUSK.**—See "Musk Artificial."

**YAMAKOSHO.**—Shinosaki (*Jour. Chem. Ind. Tokyo*, 1915, 18, 1081) has reported upon the essential oil of a plant growing in Formosa, known as *yamakosho*, and whose botanical origin is unknown. He obtained 1.2 per cent of oil from the leaves having the following characters:—

|                               |           |         |
|-------------------------------|-----------|---------|
| Specific gravity              | . . . . . | 0.9049  |
| Optical rotation              | . . . . . | — 18.8° |
| Refractive index              | . . . . . | 1.4635  |
| Ester value after acetylation | . . . . . | 48.66   |

It contains terpenes and cineol.

**YAMA-NIKKEI OIL.**—The bark of the so-called wild cinnamon or *yama-nikkei* of Japan yields an essential oil having a strong odour of camphor, and also recalling that of ginger. According to Schimmel & Co. (*Berichte*, April, 1915, 54), it has a specific gravity 0.9245; optical rotation, + 8° 34'; refractive

index, 1.47779; acid value, 0.6; and ester value, 14.8. It contains much camphor, and probably terpenes and cymene.

**YARA-YARA.**—See “Bromelia.”

**YE-SI-MIN.**—This is the local name for a Chinese plant belonging to the jasmine family. The flowers are highly fragrant, and are used for perfuming liqueurs, and possibly tea.

**YLANG-YLANG.**—See “Cananga Oil.”

**YU-JU OIL.**—According to Nagai (Publication of the Monopoly Bureau, Government of Formosa, 1914), “yu-ju oil” is a term applied to an essential oil which is obtained from the so-called “oil tree” indigenous to southern Formosa, and which is closely related to camphor oil in its properties. Its failure, however, to yield camphor in the course of production is the chief feature of difference from camphor oil, and evidently indicates the reason why the natives call the mother tree *iû-chhiu*, or “oil tree.” Similarly, the term *yu-bôku* or *yu-bun-bôku*, as frequently applied by the Japanese to the tree which yields only a little camphor and a large quantity of oil, suggests the inconspicuously small percentage of camphor obtainable.

The yu-ju tree is identical, in its external forms, with the camphor tree (*Cinnamomum Camphora* Nees et Eberm.), and the camphor manufacturers mainly rely, as the sole means of discriminating between them, upon the odour of shavings taken from the root, outside of which no particular method seems to be in current use.

Since the camphor tree growing in southern Formosa generally yields a small quantity of camphor and a copious amount of oil, it may be designated, in a comprehensive way, the “yu-ju camphor tree.” In addition to Karenkô (Hoelieng-kang) and Daitô (Tai-tang) prefectures, which possess vast growing tracts, Kagi prefecture embraces also such a district as Tanhaiku, bordering Kosempo, where the tree commonly yields six times as much oil as camphor; thus giving a fair notion of the extent to which the tree flourishes even in this prefecture. Ako prefecture also figures prominently as one of the leading producing centres. Rônô-kei (Lau-lông-khoc), Dakkô-kei (Lôk-hau-khoc), and the entire tract stretching along the Namasen-kei being the main districts.

According to the statement of a member of the Kosempo Camphor Distillery, the comparative outputs of camphor and the oil portion are at the average proportion of 25 to 75, showing that

an enormous amount of the oil is producible. In Banshōryō (Han-chû-liâu), Shinkôkô (Chhim-kau-kiu), Daipanriau (Lai-pang-liâu), and Datetsu (Phah-thih), celebrated as the chief yu-ju growing localities, some varieties often totally fail to yield stearoptene, the average yield of which generally is not more than 10 per cent. of the oil portion produced.

The yu-ju oil is readily obtained, as in the case of ordinary camphor oil, by the prevalent Tosa system. According to the investigation carried out by a member of the Kosempo Camphor Distillery, the maximum yield of camphor oil obtained from a yu-ju camphor tree in that district is 5 per cent., and a yield of 4 per cent. is considered to be fairly excellent, while the figure occasionally falls to the minimum of 1 per cent. But an average yield of 2 per cent. may be reasonably regarded as a standard.

In comparison with the Kosempo camphor oil just mentioned, the real yu-ju oil, being considered more copious in its yield, may also be safely estimated at 3 to 4 per cent. Despite the fact that the existing stocks of the yu-ju tree are much fewer than those of the yu-camphor tree, and that no large amount of production could be expected, an output of 50,000 to 60,000 kin per annum would not be a matter of difficulty.

The yu-ju oil is identical with camphor oil in physical properties, except in optical activity, in which the former seems to be slightly weaker. Usually it has a light yellow or golden or, very rarely, a greenish-yellow colour, but certain varieties of camphor oil produced from the yu-ju camphor tree growing in Kosempo frequently possess, as exceptions, an intense brown colour, or are altogether devoid of colour.

The specific gravity and optical rotation of the different varieties of the oil may be gleaned from the table on p. 839.

The oil is easily distinguished from shiu oil by the absence of the linalol colour reaction with mercuric sulphate. It contains a pinene, camphene, cineol, dipentene, camphor,  $\alpha$ -terpineol, eugenol, safrol, and possibly cadinene.

**ZATARIA MULTIFLORA.**—This is a small laëtiæ shrub found on the hills near Muscat, in Arabia. According to Sawer ("Odorographia," ii., 148), the dried plant is much used in India as an aromatic stimulant, and is sold in the native bazaars under the name *saatar*. Its fragrance is due to an essential oil which has not yet been examined.

**ZIBETHONE.**—Zibethone is a ketone isolated from civet by

# PERFUMERY

| Place of<br>origin. | No.    | Colour.                  | Specific gravity<br>at t°. | Optical rotation<br>at t°. | Refractive index<br>at t°. |
|---------------------|--------|--------------------------|----------------------------|----------------------------|----------------------------|
| Shinkôkô            | 1      | Light golden yellow      | 0.945                      | + 29.22°                   | 1.47596                    |
| "                   | 2      | "                        | 0.942                      | + 18.88°                   | 1.47457                    |
| "                   | 3      | "                        | 0.951                      | + 19.30                    | 1.47869                    |
| "                   | 4      | "                        | 0.967                      | + 22.48°                   | 1.48191                    |
| "                   | 5      | "                        | 0.966                      | + 24.42°                   | 1.48568                    |
| "                   | 6      | Golden yellow.           | 0.961                      | + 29.85°                   | 1.48045                    |
| "                   | 7      | "                        | 0.961                      | + 26.32°                   | 1.48326                    |
| "                   | 8      | Light golden yellow      | 0.963                      | + 26.95°                   | 1.48326                    |
| "                   | 9      | Golden yellow.           | 0.955                      | + 25.35°                   | 1.47850                    |
| "                   | 10     | Light golden yellow      | 0.947                      | + 27.30°                   | 1.47567                    |
| Dauparau.           | 11 (a) | Slightly greenish yellow | 0.954                      | + 21.00°                   | 1.47694                    |
| "                   | 11 (b) | "                        | 0.953                      | + 21.30°                   | 1.47694                    |
| "                   | 12 (a) | "                        | 0.972                      | + 30.80°                   | 1.47746                    |
| "                   | 12 (b) | Light golden yellow      | 0.951                      | + 28.30°                   | 1.48278                    |

## PERFUMERY

Sack (*Chem. Zeit.*, 1915, **39**, 538). It has the formula  $C_{17}H_{26}O$ , and its characters are as follows:—

|                                   |                 |
|-----------------------------------|-----------------|
| Boiling point . . . . .           | 342° at 741 mm. |
| Melting point . . . . .           | 32.5°           |
| "    "    of oxime . . . . .      | 92°             |
| "    "    semicarbazone . . . . . | 187°            |

(See "Civet.")

**ZINGIBER.**—See "Ginger."

**ZINGIBEROL.**—See "Ginger."

**ZIZIPHORA TENUIOR.**—This plant is, according to Sawer ("Odorographia," ii., 149), a native of Persia and Baluchistan, and is sold in the Indian bazaars under the name *Mishk-i-taramashia*. The Mahomedans of the East consider the plant to be the wild thyme of the Greeks. In Shiraz it is called *rang*. The odour of the plant resembles that of peppermint.



